Synthesis and modification of polyethylene powders for the use in powder bed fusion based additive manufacturing

Dissertation

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List of Publications

1. Markovnikov at Gold: Nucleophilic Addition to Alkenes at Au(III)

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2. Additive manufacturing of PA12 carbon nanotube composites with a novel laser polymer deposition process

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- Laser powder bed fusion of ultra-high molecular weight polyethylene (UHMWPE) using near-infrared ultrashort laser pulses
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List of Abbreviations

AM	additive manufacturing
BIP	bis(imino) pyridine
CAD	computer aided design
CCTP	coordinative chain transfer polymerization
СТА	chain transfer agent
DSC	differential scanning calometry
EPR	electron paramagnetic resonance
ffc	ratio between the major consolidation
	stress and the cohesive strength of a
	powder
F _H	attractive forces between a host particle
	and a wall
Fraunhofer IAPT	Fraunhofer Einrichtung für additive
	Prozesstechnologie
HDPE	high density polyethylene
LDPE	low density polyethylene
LLDPE	linear low density polyethylene
Μ	average molecular weight
МАО	methylalumoxane
Mn	number average molecular weight
NMR	nuclear magnetic resonance
PBF	powder bed fusion
PDI	polydispersity index
PE	polyethylene
ppm	parts per million
r	radius
SEM	scanning electron microscope
SLS	Selective Laser Sintering
Т	temperature
UHMWPE	ultra high molecular weight polyethylene
vs.	versus
σ _c	unconfined yield strength

1. Summary

The aim of this study was the preparation of suitable high-density polyethylene/ultra-high molecular weight polyethylene/disentangled ultra-high molecular weight polyethylene (HDPE/UHMWPE/dUHMWPE) composite powders for HDPE/UHMWPE parts by Powder-Bed-Fusion (PBF). The approach comprised of I) the preparation of HDPE, UHMWPE and dUHMWPE composite powders by the polymerization filling technique, II) the scale-up to ~ 500 g, III) screening the powders in the PBF process, and IV), evaluating the sintering/melting in the part production.

Initially, the synthesis of a catalyst capable of producing disentangled UHMWPE was developed. The synthesis of the dUHMWPE was achieved by employing 2,6-bis[1-(2,6dichloride dipropenylphenylimino)ethyl]pyridine iron(II) as precatalyst. This new Bis(imino)pyridine-iron catalyst (BIP-iron-catalyst) is a favorable alternative to the commonly used titanium-based catalysts for preparing dUHMWPE. The advantages lie in the easy synthesis of the ligand and the handling of the final catalyst. The formation of dUHMWPE was confirmed by differential scanning calorimetry (DSC), rheology and stretching experiments. The activities were high, between 1.5 to 7.4 t/(mol*bar*h) on a 40 g scale (M_w of 1-3.10⁶ g/mol), albeit with the restriction that the particle morphologies are not suitable for the PBF process. A general suitability of dUHMWPE for the PBF process could be established. The catalyst template/replication effect of heterogenized catalysts was used to generate polymer particles suitable for the PBF process. Tailor-made catalyst templates in the lower micrometer range were obtained by spray-drying silica dispersions, yielding spherical silica microparticles. These microparticles were used with an adapted strategy of the incipient wetness method for catalyst supporting, which was identified as the most useful catalyst activation and application strategy. Appropriate choice of polymerization reaction conditions allowed for the generation of silica templated HDPE and dUHMWPE particles with monomodal particle size distributions, with a median particle size of ~100 µm. Core shell HDPE@UHMWPE (scale up to ≈ 300 g) particles with a ~10 µm shell could also be generated by using a catalyst support prepared by silica coating of a commercial UHMWPE powder. DSC measurements of the powders showed a small sinter window (15-4 °C). Flowability, as measured as the ratio between the major consolidation stress and the cohesive strength of a powder (ffc), of the synthesized powders was low (ffcs of 1 to 3 in a ring shear tester) but could be increased with the addition of 1 wt% nanosized silica and 0.25 wt% carbon black (ffcs up to 6; carbon black was also a laser light absorber). All powders could be recoated at the operating temperature of a modified EOS P390 and tensile test specimens could be printed. SEM imaging revealed the general feasibility of layer wise building with these powders. Remaining challenges are control over caking, increasing the interlayer adhesion and decreasing porosity.

2. Zusammenfassung

Ziel dieser Arbeit war die Herstellung von neuen HDPE/UHMWPE/dUHMWPE Komposit-Pulvern für die Herstellung von HDPE/UHMWPE Bauteilen mittels PBF. Der Ansatz zur Herstellung dieser Komposite umfasste I) die Synthese von HDPE, UHMWPE und dUHMWPE mittels der *polymer filling technique*, II) die Maßstabsvergrößerung in den ~ 500 g Maßstab, III) das Testen der Pulver in dem PBF-Prozess und IV) das Untersuchen des Sinterns/Schmelzens der Komposite im PBF-Prozess.

Die Synthese eines Katalysators, welcher die Herstellung von dUHMWPE ermöglicht wurde mit dem Einsatz von 2,6-bis[1-(2,6-dipropenylphenylimino)ethyl]pyridin Eisen(II) Dichlorid erreicht. Dieser neu entwickelte Katalysator weist einige Vorteile zu den bisherig verwendeten, auf Titan basierenden, Katalysatoren auf: I) Die Rohstoffe sowie die Synthese sind weniger kostenintensiv, II) die Synthese des Katalysators umfasst weniger und einfachere Prozessschritte und III) der Katalysator ist weniger empfindlich gegenüber Umwelteinflüssen und somit einfacher in der Handhabung. Unter Verwendung des neuen Bis(imino) Pyridin-Eisen(II) Katalysators konnte dUHMWPE mit Aktivitäten zwischen 1.5 bis 7.4 t/(mol*bar*h) im ~40 g Maßstab (M_w of 1-3·10⁶ g/mol) synthetisiert werden. Die Bildung von dUHMWPE konnte durch DSC, Rheologie und Streckversuche bestätigt werden. Die initial hergestellten Partikel wiesen, aufgrund ihrer unregelmäßigen Morphologie, noch keine zufriedenstellende Verstreichbarkeit im PBF-Prozess auf. Es konnte jedoch eine generelle Eignung für den PBF Sinterprozess festgestellt werden. PBF geeignete Pulver aus sphärischen Partikeln konnten, durch ausnutzen des Katalysator-Templat/Replikat-Effekts der heterogenen Katalyse, synthetisiert werden. Maßgeschneiderte Katalysatorträger, aus sphärischem Silica im Mikrometer Bereich, wurden durch die Sprühtrocknung von Silica-Dispersionen erreicht. Mit der Identifizierung einer adaptierten Variante der incipient wetness Katalysatorimmobilisierungsstrategie als erfolgreichste Strategie, konnten die sphärischen Silica-Partikel mit Katalysator beladen und aktiviert werden. Der Einsatz von passenden Reaktionsbedingungen während der Polymerisation führte zu sphärischen HDPE und dUHMWPE Partikeln mit monomodalen Partikelgrößenverteilungen, mit einer mittleren Größe von~100 µm. HDPE@UHMWPE Kern/Schale Partikel mit einer ~10 µm Schale konnten ebenfalls bis zu einer Menge von ~300 g pro Batch hergestellt werden, indem mit Silica überzogene kommerzielle UHMWPE Partikel als Katalysatortemplate verwendet wurden.

DSC Messungen an allen Pulvern offenbarten kleine Sinterfenster (4-15 °C). Die Fließfähigkeit der synthetisierten Pulver war niedrig (ffcs zwischen 1 und 3), konnte jedoch unter Einsatz von 1 wt% nano Silica als Abstandshalter und 0.25 wt% Ruß als Laserabsorptionsadditiv erhöht werden (bis zu einem ffc von 6). Diese beschichteten Pulver wurden daraufhin im PBF-Prozess getestet. Alle hergestellten Pulver ließen sich bei den PBF-Prozesstemperaturen in einer modifizierten EOS P390 ausstreichen und es konnten Zugprüfkörper hergestellt werden. SEM

Analyse zeigte die generelle Durchführbarkeit von einem schichtweisen Aufbau mit diesen Pulvern. Verbleibende Herausforderungen sind die Kontrolle über zusammenbackendes Pulver abseits der belichteten Bereiche, schlechtes Haften zwischen belichteten Schichten in Z-Richtung und verbleibende Porosität im Bauteil.

3. Introduction and background

3.1 Powder bed fusion

Powder bed fusion (PBF), also known as selective laser sintering (SLS), is a sintering process which operates without the hitherto need of high pressures or long reaction times of conventional sintering.¹ As most additive manufacturing processes, it is based on a layer wise growth (Figure 1).



Figure 1: Schematic PBF process: a) vertically movable platform b) powder bed c) laser source d) laser optics e) powder hopper f) recoater for distribution and leveling²

In this case the building process consists of four steps. The first step is the application of a thin (120 μ m to 200 μ m) layer of material powder on a build platform. This is facilitated by a recoater (either a blade or roller) moving across the building platform and pushing a small amount of deposited powder in front of it, leaving behind a smooth powder layer. The next step is the heating of the powder surface with IR radiation close to the melting temperature of the material in question.³ This has the advantage that the needed energy for consolidation supplied by the laser is as low as possible and the thermal stress inflicted by the rapid heating and cooling is low.^{4,5} This step is followed by the irradiation with a laser. The irradiation leads to the

consolidation of the powder, which cools down and hardens, leaving a consolidated 2D slice of the desired computer aided design (CAD) model in the powder surface. The last step is the lowering of the build platform by exactly the height of a new layer. The steps are repeated, and the layers of the consolidated material are joined together to form the desired built part. After the building process is finished and the building chamber has cooled down the built part can be extracted from the powder bed. This process has several advantages: No support structures are needed as the unconsolidated powder in the powder bed acts as support structure. The PBF process facilitates the production of complex, kinematic parts which cannot be produced likewise with conventional formative methods. Due to the powder bed receiving a new powder layer after each laser irradiation more than one model can be built in the same building space, stacking the models. However, the process also has several disadvantages. As with all additive manufacturing techniques, the produced parts can suffer from mechanical anisotropy, due to the layer wise growth of the built parts.⁶ Additionally, the built parts often have a rough surface finish reminiscent of the powder it was created from. As the laser irradiation represents a high thermal gradient, residual stresses can result in warpage, or in extreme cases, breakages of the built parts. Due to the powdered nature of the build material residual porosity in the finished parts cannot completely be avoided.³ In parts that are subjected to mechanical stresses, these porosities can act as break initiators in other cases where a high surface area is wanted (scaffolds, membranes) a certain degree of porosity is of advantage.

Because of its attractive mechanical properties and favorable behavior in the LPBF laser sintering process, PA12 has been the most commonly used polymer in PBF processes with a market share of over 90%.⁷ PA12 has good mechanical properties, low water uptake and a low melting point, compared to other polyamides, which makes it an interesting engineering polymer.⁸ The high state of development of the PA12 based PBF processes yields built parts comparable to injection molded specimen in tensile stress and elastic modulus.⁹ PA12 powder has become the gold standard for most PBF based processes. Other polymeric materials available for PBF are depicted in Figure 2.



Figure 2: Polymeric materials available for PBF²

The main disadvantage of PA12 is its higher price compared to other commodity polymers, such as polyolefins (Figure 3). A very interesting polymer in this context is ultra high molecular weight polyethyene (UHMWPE). Its origin as a polyolefin classifies it as a commodity polymer but its good mechanical properties classify it as an engineering polymer. Regarding the prominence of PA12 on the international market, a main driver in research is to make economical more viable polyolefin polymers such as UHMWPE available for the PBF process.



Figure 3: Market overview and comparison between PBF polymers and conventional polymers¹⁰

3.1.1 Powder requirements

The PBF process has several steep requirements for a material to be used as PBF material. Not only do the bulk materials decide over the part properties but the powder properties influence the properties of the built part (e.g. accuracy, internal stress, distortion). Different powders of the same bulk material with different flowability, morphology, melting or sintering behaviors will drastically influence the outcome of the PBF process. The intrinsic and non-intrinsic powder properties affecting PBF performance are displayed in Figure 4. The most important factors influencing the PBF process can be elucidated by analyzing the steps of the PBF process.²



Figure 4: Material properties needed for successful transfer of a polymer to a PBF (SLS) capable $polymer^3$

3.1.1.1 Thermal properties and sinter window

To successfully manufacture parts out of a powder with PBF, the powder must have a certain set of thermal properties to ensure homogenous solidification of the powder. The solidification process is a complex process depending largely on the materials used.¹¹ In the case of polymeric materials the sintering is based on the liquid sintering process where the material is partially or completely molten.¹² The behavior of the molten material is then mainly governed by the capillary forces and its viscosity. When a low amount of material is melted it forms neck formation between particles. This leads to a porous built part. With increasing amount of molten material, a denser part is received. The most critical part in the PBF process is to control the

crystallization. In an ideal PBF powder the onset of melting upon heating and the onset of crystallization upon cooling are up to 30 °C apart (Figure 5).



Figure 5: DSC Measurements with sintering window (PA12)¹³

This temperature region between the two onsets is called the sinter window. The establishment of a suitable sinter window with DSC measurements is one of the first steps in establishing PBF processability.¹⁴ In an ideal PBF process, the powder is kept at a temperature above the onset of crystallization during the build job. The short term laser irradiation then elevates the powder temperature over the melting temperature and the powder solidifies without crystallization. Crystallization is then ideally initiated by the slow cooling of the whole build chamber leading to evenly distributed crystals. Two major build defects can be attributed to inhomogeneous crystallization (Figure 6). The first defect is the immature crystallization of a freshly molten layer of powder called curling. The crystallization leads to a shrinkage of the layer and thusly to stresses inside the layer, causing the edges to curl upward.¹⁵ If the curling is not too severe (e.g. higher than a new layer of powder) the next layer of powder can correct this fault. Nevertheless, this building defect leads to a deviation of the CAD model in z-direction. The second defect occurs later in the build job when inhomogeneous crystallization leads to residual stresses in the complete part and warps it. This second defect cannot be corrected and can only be seen after the build job is completed.^{3,15} Warpage represents an immense disadvantage in terms of cost and time efficiency. To prevent warping a controlled cooling rate is necessary.^{16,17} As a rule of thumb, the printed parts are cooled down as long as the building job takes to complete. Several attempts at simulating warpage with finite elements methods

were undertaken.¹⁰ Such a simulation would offer the opportunity to predict and prevent warpage or to devise countermeasures against it.²



Figure 6: Differences in dimensional deviations: Curling and warpage¹⁸

3.1.1.2 Powder flowability

A key factor in producing a PBF-capable polymer powder is the flowability of the powder. Several polymers, which can be laser sintered, are not able to be used in a PBF process, due to the insufficient flowability and packing density of the powders. The most critical step is the deposition and smoothening of a single powder layer. The success of this process depends largely on the particle morphology. The more spherical and smooth the single particles are the better they can glide off of each other, resulting in a better overall powder flow and packing density.¹⁹ Irregular powder suffer in flowability with increased packing density (interlocking).⁹ The attractive forces that act on the particles are the combined van der Waals, electro static and liquid bridge forces (e.g. residual moisture). The order of magnitude of their effects depending on the particle size are depicted in Figure 7 in a simple model, where a particle is interacting with the surrounding wall. The liquid bridges have the biggest influence on the attractive forces, followed by the van der Waal forces and electrostatic forces.²⁰ As the PBF process mostly operates at higher temperatures than 100 °C liquid bridges consisting of water can be neglected but can be an issue at room temperature flowability measurements. This can lead to higher recorded flowability values at elevated temperatures.²¹ It can be clearly said that the van der Waals forces are the most dominant attractive forces at play in a PBF powder especially for powders with a share of fine particles.



Figure 7: Influence of the particle size on the attractive forces between a wall and the particle²⁰

Several flowability test methods are available. The best results in terms of predictable PBFsuitability can be achieved with the measurements mimicking the process conditions as close as possible. A consensus of which test methods yield the best results in PBF suitability has not been reached.

The most simple flowability measurements are funnel based flowability tests (HALL flow meter ASTM B213, Carney Funnel ASTM B964). In these tests a powder is placed inside a funnel and the time needed to flow through an orifice is measured. The advantage of these tests lies in their simplicity and cheapness. These types of tests are better suited for good flowing powders (metal) than for powders that are cohesive, but they still work in AM (polymeric powders).²² Due to high errors in the measurements (operator influence, aeration of powders) the results of these tests can only be used for comparative tests and not for quantification statements.²³ Another very easy method is the HAUSNER ratio (HR) (ASTM D7481-09). The Hausner ratio is defined by the ratio of the bulk and the tap density of a powder. A HAUSNER ratio of 1 identifies a powder as incompressible. The view on the HAUSNER ratio in the literature is divided. SPIERINGS et al. mention that the HAUSNER ratio cannot be correlated well with other more sophisticated flowability measurements and is therefore not suited for the PBF powder characterization.²² Other authors were able to distinguish several grades of PBF powders using the HAUSNER ratio.²⁴ A similarly divided case can be found for the also widespread measurement of the angle of repose of a bulk solid. It seems to be useful for free flowing to slightly cohesive powders but fails for the cohesive but still usable PBF powders.^{23,25} This method again suffers from operator influence. Of the more advanced flowability measurements powder rheology has become popular in recent years.²⁶⁻²⁸ This method operates on the

principle of a mixing element displacing powder and measuring the forces needed to do so. All the rheological parameters (stability index, specific energy, conditioned bulk density) obtained with a Freeman FT4 rheometer correlated well with the actual PBF recoater performance. Similar attention has been received by the dynamic avalanche angle measurements. This method is based on measuring the dynamic avalanche angle of a powder inside a rotating drum. It could be shown that this method is useful for determining the PBF suitability with the measured flow properties (avalanche flow index, cohesive index, surface fractal).^{22,29} Proponents of this method indicate the likeness of the avalanche to the likeness of the avalanche during a PBF recoating process, while opponents criticize the lack of theoretical background.^{20,30} A large group of flowability testing methods can be summarized under shear testing. One of the most prominent representative of this method is the Schulze ring shear test cell (ASTM D6773) (Figure 8).³¹



Figure 8: Schematic view of a Schulze ring shear test cell²⁰

This method relies on bringing the powdered sample in a conditioned state and testing from this conditioned state. This allows for high repeatability and high understanding of the theoretical background.²⁰ A measurement is executed as follows: A powder is placed under a predefined pressure in the ring shear tester and is sheared until homogenous flowing is achieved (preshear). The pressure is then reduced to the actual measuring pressure and the powder is sheared again until incipient flow starts. The stress required to shear the compressed powder sample is called shear point. By repeating the first step and then measuring several pressures a yield limit/yield locus can be constructed (Figure 9).²¹



Figure 9: Measurement of shear points and the construction of the yield limit²⁰

From these individual shear points Mohr circles can be constructed. These represent all forces at all angles inside the powder at the point of incipient flow. The two meeting points of the Mohr circle with the x-axis represent the forces applied from the top and from the sides (σ_1 , σ_2). By constructing a Mohr circle that exhibits a crosspoint directly at the origin (representing no side forces) the unconfined yield strength σ_c can be determined.



Figure 10: Yield locus and Mohr stress circles²⁰

To numerically determine the flowability the ratio ffc of the consolidation stress, σ_1 at the preshear condition to the unconfined yield strength σ_c is used. The larger the ffc the better a powder flows. The ffc can be defined in the following regions of flowability.

ffc<1	Not flowing
1 <ffc<2< td=""><td>Very cohesive</td></ffc<2<>	Very cohesive
2 <ffc<4< td=""><td>Cohesive</td></ffc<4<>	Cohesive
4 <ffc<10< td=""><td>Easy flowing</td></ffc<10<>	Easy flowing
10 <ffc< td=""><td>Free flowing</td></ffc<>	Free flowing

Table 1: Flow behavior for different ffc values

Opponents of this technique find it not comparable to the PBF process, as the powders are measured under a compressive load.²² Proponents point out that the technique is able to work under minimal compressive loads (as low as 500 Pa) and has been successfully used to identify different qualities of PBF powders with different kind of shear cells.³²

3.1.1.3 Optical properties

The absorption of the used laser by the powder must be sufficient for a successful PBF process. Next to the absorption, the refraction and reflection of the powder must be taken into account. Ideally, the energy supplied by the laser is absorbed directly and only at the focus point of the laser beam. Increased interaction through refraction and reflection decreases the spatial resolution of the building process as material outside of the laser path is influenced. To control the absorptivity of a powder additives such as carbonaceous compounds, can be employed.² A close-up of the line-by-line consolidation can be seen in Figure 11. The depth, width and overlap of the consolidated line left by the traveling laser focus in the powdered material is dependent on the PBF parameters laser power, scanning speed and hatch spacing.



Figure 11: PBF process parameters³³

3.1.1.4 Additives

Several types of additives/filler systems have been investigated to adjust PBF powder properties (mainly for PA-12). Additives or fillers can be put in two categories: Those that increase the processability of the polymer in a SLS-process (flowability, particle shape, melt viscosity, surface tension, crystallization) and those that are used to increase key properties of the sintered product (stiffness, mechanical strength, fire retardance, biocompatibility, conductivity. etc).² Ideally, filler systems have positive influences on both categories. To increase absorption of the used laser wavelength the addition of dyes^{34,35}, carbon black,³⁶ phosphates,³⁷ or carbon nanotubes^{38–41} have been investigated. Increasing the absorbance leads to less transmittance through the powder layer to already sintered parts. Better conversion of laser- to heat-energy also means less laser-energy is needed for melting, resulting in less radiation induced side reactions. Another technique to increase thermal and mechanical strength of the sintered product is the introduction of heat and light conducting/refracting/diffracting filler (carbon nanotubes⁴², glass beads^{43,44}). Distributing the laser energy evenly over the irradiated surface is important in reducing thermal stress (gaussian energy profile of laser spot) and increases the sintering between neighboring particles.

A common Problem of PBF powders, which can be solved by additives, is the insufficient flowability of the base materials. To increase the flowability of PBF powders nano-sized spacers are employed. As the attractive forces between particles are dependent on their distance, introducing these spacers greatly reduces the attractive forces. The effect is

dependent on the difference in size between the space and the host particle, as well as the surface covering of the host particles. A reduction in attractive forces is most efficient if the particles are small enough (nano-sized) so that their own attractive forces do not have a large influence on the overall attractive forces (Figure 12).



Figure 12: Influence of the radius *r* of a spherical flow additive on the attractive forces (F_H) between a host particle and a wall²⁰

3.1.1.5 PBF powder production

The PBF process requires high control of particle size distribution and particle morphology in the production of polymeric PBF powders. Industrially manufactured powders usually have a size range of 60 µm and a narrow particle size distribution.¹² The chosen production process of PBF powders is dependent on the material used and the desired powder properties needed. Three industrially used techniques have been developed to produce PBF powders: I) Cryogenic milling of bulk material; II) Precipitation of polymer solutions; III) Co-extrusion of non-miscible polymer blends.

Cryogenic milling involves cooling the bulk polymer below their glass transition point and crushing the material with an impact crusher to receive powders in the 100 µm range. This process yields jagged and uneven particle morphologies with a broader particle size distribution, which do not flow well. Nevertheless, this process is one of the most economical and simple procedures to produce PBF powders. The addition or mixing of components and additives is very easy in this process and can lead to mechanical alloying of the components (e.g. PA12 and PEEK⁴⁵). A common technique to alleviate the undesired morphologies and the broad particle size distributions is to introduce the milled powders to a downer reactor, where the particle edges are rounded by hot gas, and then to implement a sieving process to control the particle size distribution.

Precipitating out of polymer solutions is mainly used for polyamide PBF powders. In such an exemplary process, polyamide 12 is dissolved at elevated temperatures in ethanol. Upon cooling down the polyamide separates out of the solution and forms 50 µm - 150 µm large, non-porous particles with a narrow particle size distribution. The morphology is not perfectly round, but more potato shaped, yet still usable in PBF processes. Investigation of different types of solvents and polymers is topic of scientific and industrial research. The mixture of polymers or the usage of additives is complicated in this process, as they can heavily influence the precipitation behavior (e.g. initiating nucleation or separation of compounds).

To create perfectly round and smooth PBF powders two methods are available. Both operate under the same principle of emulsion formation. The first method comprises of co-extrusion of two non-miscible polymers. The minority phase will form droplets in the matrix during the mixing action. The matrix polymer is then removed with an appropriate solvent, which must be a non-solvent for the minority polymer. After sieving and drying the resulting minority phase polymer PBF powder is obtained.⁴⁶ A good example of this technique is the production of isotactic polypropylene PBF powder with polyvinylalcohol as matrix and water as matrix removing solvent. This process is quite costly and is only economically viable because of the superior powder properties. Another more economically viable route to perfectly round and smooth polymer particles is the production of polymer powders from a monomer emulsion.^{2,3} This route is limited to emulsifiable monomers. A good example is the production of polystyrene PBF powder from a styrene/water emulsion.^{2,10} SEM analysis of the different morphologies, resulting from the different production techniques, is depicted in Figure 13.^{2,10}



Figure 13: Morphologies of commercial powders for PBF. a: Cryo milled particles (EOS GmbH: PA-11 PA1101) b: Precipitated particles out of PA12 (EOS GmbH: PA2200) c: Polystyrene particles produced by emulsion polymerization (EOS GmbH: PS powder PrimeCast)²

Several other techniques for the production of PBF powders are known, such as spray drying,⁴⁷ wet grinding,⁴⁸ fiber cutting⁴⁹ and solubility of supercritical gas in a polymer melt.⁵⁰

3.2 Polymerization of ethylene

3.2.1 Molecular structure, molecular weight distribution and resulting material properties

The most common classification system for polyethylene is based on bulk density. High density polyethylene (HDPE) has a median density greater or equal to 0.941 g/cm³, while low density polyethylene (LDPE) has a density between 0.910 g/cm³ and 0.940 g/cm^{3.51} Perfectly amorphous polyethylene would have a density of 0.880 g/cm³ while a complete polyethylene crystal would have a density of 1.000 g/cm^{3.52} These differences in densities arises from their different crystallization behavior due to the different microstructure of LDPE vs. HDPE. HDPE consists out of single chains of polymer without any branches, whereas LDPE consists out of chains with side branches of up to 50 ethylene units with possible short sub-branches. These side branches make it harder for the LDPE to settle into a perfect crystal and thus a higher percentage of LDPE stays amorphous after cooling from the melt.⁵³ A third common type of polyethylene is the linear low density polyethylene (LLDPE). LLDPE is generated by incorporation of 1-olefins into the polymerization and has a similar density to LDPE. A graphic representation of a lamellar polyethylene crystal and the different types of polyethylene is pictured in Figure 14.



Figure 14: Representation of a lamellar folded polyethylene crystal and schematic representation of different types of polyethylene^{53,54}

The material properties hardness, brittleness, melting point and glass transition point are depending on the amount of crystallinity and molecular weight of the polyethylene.⁵⁵ In Figure 15 the resulting mechanical properties are depicted and classified into substance applications.



Figure 15: Crystallinity plotted vs. the molecular weight and the resulting mechanical classification by aplication. *Winothenes®* and *Alkathenes®* are registered trademarks⁵⁵

In the low molecular weight regimen the crystallinity changes the mechanical properties from very soft (greases) to soft but still pliable (soft waxes) to ultimately hard and brittle (brittle waxes). Increasing the molecular weight increases the material properties in a similar matter (soft to hard) with a distinct difference: With longer chains the resulting material will not be brittle but flexible (plastics). Another key property that corresponds to the molecular weight and molecular structure is the zero-shear viscosity of the melt (Figure 16).



Figure 16: Left:Zero-shear viscosity plotted against the molecular weight of linear HDPE samples.⁵⁶ Right: Zero-shear viscosity of linear and long-chain branched LDPE and LLDPE samples⁵⁷

Two distinct regions can be observed in the double logarithmic graph of zero-shear viscosity plotted against the absolute molecular weight of linear polyethylene. The first region spans from zero to ~ 2000 g/mol. The behavior of the samples can be accurately described with a linear regression with a slope of one.

Above ~2000 g/mol the data points can equally be accurately fitted with a linear regression with a slope of 3.6. Slight deviations from the fit are due to broad or bimodal molecular weight distributions.⁵⁶ The molecular weight at the intersection of both linear regressions is known as critical molecular weight. It marks the transition between the two regions. This behavior can be attributed to the reputation theory first published by DE GENNES.⁵⁸ At the critical molecular weight the chains are beginning to be hindered by entanglements with itself and other chains. Lateral chain movements are not possible anymore and the only movements are snake-like reptations along the axis of the polymer chain. According to DE GENNES the relaxation time is defined as the time a chain needs to move once its entire length. This relaxation time is depending on the third power of the molecular weight. This description is close to the actual measured values of 3.4 to 3.6.

The behavior of long-chain branched or star-polyethylene is markedly different (Figure 16, right). It can be observed that the data points cannot be fitted with a linear regression any longer. Different approaches have been made to develop a good fit function depending on the side branch structure and length.^{59–61} It is important to note that these star- or long-chained-polyethylenes have a much higher sidechain ratio and length as in commercial available LDPE or LLDPE. LDPE and LLDPE with a side-chain ratio found in commercial products can also be accurately described with the linear regression found for linear polyethylenes.⁵⁷



Figure 17: Reptation model according to DE GENNES and graphic interpretation of the entanglement molecular weight $^{\rm 62}$

The statistical chain length between two entanglement points is called the entanglement molecular weight. The rule of thumb "Three fingers hold a stick" describes the dependency between the entanglement molecular weight and the critical molecular weight, as the critical molecular weight is often two to three times the size of the entanglement molecular weight.

The co-dependency of the entanglement density and the critical molecular weight of linear polymers has been studied extensively in literature.^{63–67}

Apart from the chain length and the molecular structure the molecular weight distribution has also a big effect on the resulting material properties. A narrow molecular weight distribution is not always favorable as polymers are a product which need to fill several roles in its production process. I.e. it needs a low enough viscosity to be used in molding processes and needs a high toughness to withstand external forces when cold. Both attributes can be obtained if a blend of high molecular weight for toughness is combined with a low molecular weight component generating the lower viscosity. The long chains of the high molecular weight polyethylene act as tie molecules between low molecular weight polyethylene crystals and transferring external forces from one crystal to the next, preventing cracking. Such a bimodal molecular weight distribution and resulting tie molecules is exemplary shown in Figure 18.



Figure 18: Exemplary mixture of high and low molecular weight polyethylene with long polymer chains acting as tie molecules⁶⁸

As extruder blending of high and low molecular weight polyethylene is not yet commercially viable, due to the high viscosity of high molecular weight polyethylene, and is still topic of recent research,⁶⁹ other methods are needed to intimately mix high and low molecular weight polyethylene. This feat can be accomplished by synthesizing low and high molecular weight polyethylene next to each other. This technique is called reactor blending. Several reactor blending techniques are depicted in Figure 19.



Figure 19: Left: Reactor blend technology based on multi-site catalysis and the resulting tailored molecular weight distribution. Right: Multi-reactor cascade and multi-zone reactor as additional reactor blend examples⁶⁸

The first approach uses different catalysts within one reactor system. Each catalyst is responsible for producing one part of the resulting multimodal polyethylene distribution. Another approach would be to create different reactor environments for one catalyst. E.g. the loop reactor is responsible for generating one molecular weight distribution while the fluidized bed reactor is responsible for the other molecular weight distribution. The last concept is the Spherizone concept by LYONDELBASELL.⁷⁰ In the riser and downer zones different reaction environments are present subjecting the circulating product to alternating polymer growth. Examples of effective reactor blending can be found in recent literature.^{71–75}

The catalysts used should produce as narrow as possible distributions to be able to carefully adjust the amount and length of the resulting chains to ensure these approaches can be used to its full potential. The goal is to generate the wanted properties in the final polymer product. Two types of ideal distributions are possible, depending on the reaction regimen of the polymerization. The first and more common distribution is the SCHULZ-FLORY distribution.⁷⁶ It is also called the most probable distribution and is a discrete distribution with the differential mass distribution function of the form:

$$f_{w}(x) = a^{2} x (1-a)^{x-1}$$
 Equation 1

With *x* being the parameter characterizing the chain length, e.g. relative molecular mass or degree of polymerization, and *a* being a positive empirical constant.⁷⁷ This distribution is characterized by a minimally achievable polydispersity index (PDI) of 2 and an asymmetric distribution favoring low molecular weight products. Prerequisite for a polymerization to yield a SCHULZ-FLORY distribution is the simultaneous occurrence of deactivation of active centers, yielding inactive chains, and the new formation of active centers, yielding small new chains. This behavior leads to a steady state with a stable concentration of growing chains. An example for a polymerization yielding this type of distribution is the free radical polymerization. Free radicals are generated by decomposing initiator molecules while active growing chains

can be deactivated by radical transfer reactions or by coupling with another active radical. The amount of coupling reactions determines the broadness of the resulting distribution.⁷⁸ The other most important ideal distribution is the Poisson distribution. It is a discrete distribution with the differential mass-distribution of the form:

$$f_{\rm w}(x) = \frac{{\rm e}^{-a} a^{x-1}}{(x-1)!}$$
 Equation 2

With *x* being a parameter characterizing the chain length e.g. relative molecular mass or degree of polymerization and *a* being a positive empirical constant.⁷⁹ This distribution is defined by a very narrow distribution with a PDI of 1 and a symmetrical distribution. For a polymerization to generate polymers that follow a Poisson distribution there must be no permanent deactivation of growing chains. Chain growth must not be dependent on chain length or other factors. Typical examples of polymerization generating Poisson distributed polymers are living ionic polymerizations.^{54,80}

3.2.2 High pressure synthesis of polyethylene

The most common route to synthesize polyethylene is the high-pressure synthesis. It is the oldest commercial route to LDPE originated by FAWCET at Imperial Chemical Industries in 1936.⁸¹ This route consists of subjecting the monomer ethylene to pressures between 1500 to 2300 bar and temperatures between 150 °C and 200 °C together with a radical starter, such as oxygen or peroxides. The free radical polymerization that follows must be controlled carefully to prevent an exothermic runaway. Commercial processes use tubular continuous plug flow reactors at high flow rates to generate a high surface to volume ratio using over critical ethylene as solvent. After the reaction the reaction mixture is decompressed and the residual ethylene is recycled. The resulting polymer is then processed further to generate films, tapes or granules.⁸² Due to the radical polymerization back biting and radical transfer can take place, leading to a branched microstructure of the polymer.⁸³ The chemistry and kinetics of the free radical polymerization of ethylene at high pressures is described in detail in literature.^{84–86} The nature of the radical chemistry makes it possible to incorporate a wide array of possible olefinic monomers and even more polar monomers, such as acrylates or vinylacetate.⁸⁷ This facilitates a high degree of freedom to tailor the resulting polymer properties. The high pressure synthesis of LDPE is still being used to generate LDPE in the Mt range despite the high costs of high pressures and temperatures.54,88

3.2.3 Low pressure synthesis of Polyethylene

ZIEGLER and NATTA discovered the catalytic activity of β -TiCl₃ synthesized by the reaction of TiCl4 with aluminum alkyls.^{89,90} This class of catalyst is able to generate linear HDPE In comparison to the branched LDPE synthesized by radical reactions. The reaction pathway follows the insertion mechanism first proposed by COSSÉE and ARLMANN (Scheme 1).



Scheme 1: Proposed reaction pathway for the polymerization of ethylene under the action of β-TiCl₃^{54,91}

Prior to the reaction the crystalline β -TiCl₃ particle is alkylated by aluminum alkyls yielding the catalytic active cationic species. The reaction starts with the side-on coordination of an ethylene molecule at a free coordination site at the titanium center. The next step is an insertion of the ethylene into the alkyl chain opening up a coordination site for the next ethylene molecule.⁹¹ The resulting molecular weight distributions are quite broad and the incorporation rate of comonomers is inhomogeneous, due to many active sites in one particle competing for ethylene and comonomers.^{78,92} This behavior is a hallmark of multi-site catalysis. Most HDPE polymer is produced by heavily improved and advanced versions of heterogenous catalysts based on the Ziegler-Natta catalysts.^{54,93,94}

3.2.4 Single-site catalysts

Research has been carried out to develop single-site catalysts to elucidate the relationship between the active catalyst structure and the resulting polymer properties. Other incentives to develop single-site catalysts were the hope to narrow the broad molecular weight distributions and homogenize the comonomer incorporation rates (Figure 20).



Figure 20: Typical molecular weight distributions and comonomer content of a single-site catalyst (left) and a multi-site catalyst (right)⁷⁸

First efforts in this research field have been carried out by BRESLOW⁹⁵ and NATTA⁹⁶ in 1957. The first research was based on fourth group transition metals after the success of titaniumbased heterogenous catalysts. The metallocene derivates of zirconium, titanium and hafnium were indeed suitable single-site polymerization catalysts. These catalysts had in common that they did not respond well to activation with metal alkyls. The true potential of these catalysts did manifest itself after the discovery of methylaluminoxane (MAO) as potent catalyst activator by SINN and KAMINSKY in 1976.⁹⁷ MAO is synthesized by the partial hydrolyzation of trimethylaluminum. The resulting mixture of different possible morphologies, such as chains, rings or clusters, has not been fully elucidated (Figure 21).



Figure 21: Hypothesized structures of methylaluminoxane. Structures can reach a molecular weight up to 1000 g/mol⁹⁸

Further research in the area of metallocene catalysts is mostly reserved for the stereoselective synthesis of polyethylene with comonomers or for propene polymerization to yield stereospecific polymers. The research group of BRINTZINGER developed the *ansa*-metallocenes in 1982 by connecting the cyclopentadienyl rings freezing the ligand geometry

around the active center.⁹⁹ Effective stereocontrol of the resulting polymer chain can be achieved by introducing differently sized moieties on the cyclopentadienyl ligand.¹⁰⁰ The next evolutive step was to replace the cylopentadienyl ligands to create cheaper, more robust and more active catalysts. By applying the isolobal concept¹⁰¹ a screening of appropriate ligand candidates gave the class of half-sandwich complexes. Well known isolobal replacements for cyclopentadienyl ligands are amides, ketamide, guanidinates, iminoimidazolidide, phosphinimide and aryloxides.¹⁰² Aside from changing the ligands and their geometries, research has been carried out to replace the active center towards more abundant and thusly more economic viable late transition metals. Challenges arise from the properties of late transition metals to undergo β -hydride elimination towards the metal center yielding short oligomerized 1-olefins as the main product. This property has been exploited in the SHELL higher olefin process using a Nickel(II)-complex.¹⁰³ Careful ligand selection has been carried out to suppress the unwanted β -hydride elimination to develop useful polymerization catalysts.^{54,104}

3.2.5 Coordinative chain transfer polymerization

Coordinative chain transfer polymerization (CCTP) takes the concept of single-site polymerization one step further. Instead of only one chain growing per active catalyst a chain transfer agent (CTA) is added to the reaction increasing the number of growing chains per active catalyst. A simplified reaction scheme can be seen in Scheme 2.



Scheme 2: Simplified reaction pathways for the activation, transfer, growth and termination reactions of a bis(imino) pyridine iron(II) chloride complex in a coordinative chain growth regimen^{54,105}

This reaction pathway gives a reservoir of passive "sleeping" chains which can be transferred between the active catalyst and a dormant chain transfer reagent. This can be a considerable advantage as it yields the opportunity to increase the productivity of a given catalyst molecule by producing more chains per catalyst. Depending on the CTA used follow up reactions of the CTA terminated polymers can be explored, yielding the opportunity for functionalized end-groups. If the transfer reaction is orders of magnitudes faster than the growth reaction, all polymer chains transferred between the CTA and the active catalyst will grow at the same

speed. Ideally the resulting molecular weight distribution should thusly follow a Poisson distribution.^{105–108} By carefully adjusting the reaction parameters the chain length of the polymers should also be controllable. Literature known active centers include hafnium, zirconium, actinoids, ytrium, cobalt, iron and titanium.¹⁰⁶ A wide array of ligands, such as cyclopentadienyls, aminopyridines, aminidates and bis(imino)pyridines, are reported in literature.¹⁰² Common chain transfer reagents include metal alkyls based on magnesium, aluminum and zinc.^{54,106}

3.2.6 Bis(imino) pyridine catalysts

With the discovery of the bis(imino) pyridine iron(II) (BIP) catalyst class in the 1990s, a new catalyst class was simultaneously described by BRITOVSEK *et al.*^{109,110} and SMALL *et al.*^{111,112} They are structurally neighbors to the previously discovered catalyst classes of palladium and nickel centered bis-oxazoline und α -diimine complexes.¹¹³ The newly discovered class of catalysts is based on the abundant, non-toxic element iron and yields highly linear polyethylenes while the palladium and nickel based systems are prone to chain walking and insertion of 1-olefins.^{114–119} The general structure of a symmetric BIP catalyst is shown in Scheme 3.



Scheme 3: General structure of a symmetric mononuclear BIP metal chloride precatalysts

The most common preparation pathway is the double Schiff-base condensation of 2,6-diacetylpyridine with two equivalents of appropriate aniline derivates to yield the symmetrical bis(imino) ligand.¹²⁰ The next step consists of the formation of the metal complex by introducing the metal chloride into the system. This precatalyst is activated by alkylation with short chained aluminum alkyls or MAO.

The state of the activated catalyst is still topic of scholarly debate. The most simple suggested activation pathway consists of the double halide abstraction and alkylation of the iron center yielding the cationic iron BIP species with an anionic MAO counterion. It has been shown that these types of cationic species do polymerize ethylene,¹²¹ but the complex reaction environment yields a plethora of active and inactive catalyst structures. Extensive nuclear magnetic resonance (NMR) and electron parametric resonance (EPR) studies of the group around ZAKHAROV led to the assumption that different activating reagents lead to different heterobimetallic species (Scheme 4). By using aluminum alkyls a neutral heterobimetallic complex is formed while under the action of MAO an ionic pair of a cationic BIP iron(II) structures, together with an anionic MAO molecule, is formed. These bimetallic species are
not active polymerization species. Depending on the amount of alkylating reagents this type of catalyst structure can outweigh the amount of active catalyst species resulting in a reservoir of "sleeping" catalysts.^{122–124}



Scheme 4: Schematic reaction pathways for the synthesis of heterobimetallic BIP iron complexes^{54,122}

A concentration of aluminum alkyls which is too high leads to the deactivation of the catalyst by alkylating the ligand or reducing the iron center to inactive iron(I) species. BIP iron(III) catalysts show similar to higher activities compared to their iron(II) counterparts.^{125,126} EPR and NMR studies suggest that the iron(III) species is not as stable as the iron(II) species in a reducing environment and is converted to the iron(II) species.¹²⁷

The formation of the active catalyst, originating from the heterobimetallic neutral complex, is triggered by the displacement of one aluminum alkyl molecule and the subsequent coordination of an ethylene molecule (Scheme 5).¹²⁸



Scheme 5: Formation of the active catalyst structure by displacement of one aluminum alkyl moiety by an ethylene molecule^{54,122}

The possible reaction pathways the activated catalyst can undergo are depicted in Scheme 6. The first reaction is the insertion of an ethylene molecule into the growing chain by the mechanism proposed by COSSÉE and ARLMANN.¹²⁹ The following two reactions depict the possible β -hydride eliminations. First: The β -hydride elimination towards the metal center and

second: The β -hydride elimination under the influence of an ethylene molecule. The last reaction shows the chain transfer between an aluminum alkyl and the iron center. A perfect CCTP behavior can be reached if the concentration of aluminum alkyls is high enough. All reactions have in common that they yield an active catalyst center after the reaction. σ -Bond metathesis and insertion of a 1-olefin higher than propylene¹³⁰ have not been observed with this catalyst class.



Scheme 6: Reactions of the activated catalyst^{54,110}

BIP complexes with a major part of the periodic table of elements have been discovered.¹²⁸ Activity towards the polymerization of ethylene can be observed when using BIP-complexes of late transition metals such as chromium, vanadium, nickel, and cobalt. These coordinated metal ions yield catalysts which do not reach the same activity and selectivity towards saturated chain termination as iron based BIP catalysts. Apart from the choice of the coordinated metal ion the most influence over the polymerization can be gained by the structure of the ligand. Changing the size of the ortho moieties on the aryl rings influences the selectivity of the catalyst. Choosing small methyl moieties on the aryl moieties leads to highly active catalysts that terminate the chains mainly by β -hydride elimination.¹³¹ Increasing the size of these ortho aryl moieties decreases the activity and leads to longer saturated chain termination. Mixed or asymmetric catalysts often lead to highly active catalysts producing short chained 1-olefins. This behavior is due to the steric control around the active site. Especially the six membered ringed transition state of the β -hydride elimination towards ethylene is sterically demanding.¹³² This reaction pathway can be effectively closed off by steric crowding the active site over and under the coordination plane of the planar BIP three pronged basic structure. The reaction then terminates with a higher probability towards aluminum or not at all resulting in longer chains. Apart from the steric influence of the aryl bound moieties the effect of electron pushing or pulling moieties can be observed. An increase in catalytic activity can

be observed if the slightly electron donating alkyl moieties are exchanged with electron pulling halogen atoms. This is due to the overall weakening of the ligand metal center bonds.¹³³ Reducing the steric bulk of the aryl rings at the imine moiety leads to deactivated catalysts by bis chelating ligands.¹³⁴ Changing the methyl moiety at the imine structure towards sterically demanding ligands reduces the overall catalyst activity immensely. Reducing the methyl moiety to a single proton yields an active catalyst which produces mainly 1-olefins.⁵⁴ Main parameters influencing the polymerization outside the choice of catalyst are described below.

Concentration of chain transfer reagent

Increasing the concentration of chain transfer agent leads to a more narrow distribution of molecular weight of the resulting polymer as higher frequencies of transfer lead to a homogenous growth of almost all polymer chains at the same time, as long as no precipitation of aluminum polymeryls takes place. High concentrations of CTA can lead to bimodal molecular weight distributions, due to aluminum polymeryls dropping out of solution and not participating in further transfer reactions.¹¹⁰

Concentration of monomer

Increasing the monomer concentration leads to a linear increase of yield of polyethylene as the reactions of insertion and growth and the β -hydride elimination are favored over the chain transfer reaction.¹¹⁰ Graphic representations of the monomer concentration and the concentration of CTA on the reaction rates of the transfer, β -hydride elimination and the growth reactions are depicted in Figure 22.



Figure 22: Schematic plotting of reaction rates vs. reaction time in different reaction scenarios using MAO as activator and CTA in a CCTP with BIP iron complexes. A: Low concentration of CTA. B: High concentration of CTA. C: High ethylene pressure. D: low ethylene pressure¹¹⁰

Temperature

Increasing the reaction temperature leads to a deactivation of the active catalyst possibly attributed to rotation of the aryl moieties sterically opening the catalyst center for side reactions.¹²⁸ This leads to shorter chains and lower overall activity. This can be seen as an inherent safety feature as exothermic runaway reactions with catastrophic outcomes are not possible.¹¹⁰

Time

The chain transfer reaction is the most influenced reaction by the reaction progress as the increasing chain length transferred on to the aluminum atom decreases its mobility and increases its steric hindrance. The reaction rate decreases drastically over time while the growth and β -hydride elimination are not affected, leading to a stagnating amount of low molecular weight polyethylene while the high molecular weight fraction keeps increasing.^{54,110}

3.3 UHMWPE and disentangled UHMWPE

Ultra high molecular weight polyethylene is a type of HDPE with elevated molecular weight. The most common definition of UHMWPE is a polyethylene with a molecular weight in excess of 1x10⁶ g/mol. The viscosity of the melt of such an UHMWPE can be as a high as 10¹⁰ Pa*s, due to the high amount of entanglements in the linear UHMWPE chains. The high melt viscosity prevents the usage of the Polymer processing techniques of injection molding or screw extruding.^{135–137} Nevertheless, this polymer is widely used as it is cheap in production and has outstanding physical properties, such as high abrasion resistance, high impact resistance, fatigue resistance, self-lubrication, a good resistance against low temperatures, high chemical stability and chemical inertness.^{138–140} Its property profile situates UHMWPE at the border between commodity polymers and engineering polymers.

Parts, especially profiles such as rods or plates, out of UHMWPE are commonly produced by continuous ram extrusion of powdered UHMWPE. More intricate parts, such as artificial join replacements, are directly pressed into the desired shape by compression molding of UHMWPE powder in a discontinuous process. Both techniques often require further annealing or subtractive machining to generate the final desired parts. Extensive studies have been executed to understand the impact of fabrication conditions, post-molding treatment, machining and powder morphology on the final parts.^{141–147}

These rather expensive processing techniques are quite restricted in their abilities to produce complex shapes. Additive Manufacturing (AM) of UHMWPE with powder bed fusion would offer the possibility to generate tailor-made complex shapes in a quick and economical process.

In the last years, more and more research into PBF with UHMWPE has been carried out.^{148–}¹⁵² The received parts of PBF built UHMWPE are not yet comparable to traditionally manufactured parts of UHMWPE. Warpage and shrinkage are often found, due to the insufficient crystallization management, possibly due to the thermal mismanagement in the build chamber. As the actual melting or sintering process takes place in a short amount of time, the entanglement of the chains between themselves and neighboring chains is often incomplete, due to the long reptation time needed by the long UHMWPE chains. This results in inferior mechanical properties compared to traditional manufactured UHMWPE parts.^{58,153}

Disentangled UHMWPE is a type of polyethylene, which consists out of single polymer chains folded into crystals with minimal inclusion of different chains. It can be found in nascent UHMWPE, where the reaction parameters (living catalyst at low catalyst concentrations and low reaction temperatures^{72,154}) ensure a higher rate of crystallization than entanglement.^{155–157} Melting the disentangled UHMWPE results in a heterogenous melt with partially entangled and disentangled chains.

Depending on the parameters of the melting process (heat rate, shear rate, time) the disentangled state is lost, and a thermodynamically stable entangled state is reached. This phenomenon is accompanied with an increase in modulus and viscosity buildup.¹⁵⁸

Hot press sintering studies^{159,160} of nascent disentangled UHMWPE powder has led to the discovery of yet another property coined *melting explosion*. Polymer chains entangled faster and more profound than can be explained through reptation alone. Several authors suggest sideways or segmental motion or cooperative ROUSE motions of the polymer chain at the scale of the gyrational radius, leading to a fast entropically driven entanglement between particles and chains.^{145,161–163} Therefore, UHMWPE parts sintered from disentangled UHMWPE show a dramatic increase of mechanical strength and high draw ratio (50% to 500 %) compared to parts prepared from entangled UHMWPE.^{158–160}

3.4 Supported catalysts and catalyst templates

Almost since the first discovery of homogeneous catalyst systems efforts into their heterogenization have been explored. The driving forces behind these efforts are the reduction of reactor fouling and the control over the bulk density and the morphology of the resulting polymer.¹⁶⁴

Most commonly used materials for catalyst supports are inorganic materials, such as silica-, alumina- or magnesium dichloride-particles.¹⁶⁵ The fixation of the catalyst can either be performed by a physical absorption, electrostatic interaction or a chemical reaction.¹⁶⁶ The interaction between catalyst support and catalyst can be complex and lead to a plethora of different effects. An overview over the parameters influencing polyolefin production with a heterogenized catalyst is given in Figure 23.

Molecular Weight (MW)

Molecular Weight Distribution (MWD)



Figure 23: General parameters influencing the synthesis of polyolefins with supported catalysts¹⁶⁷

For the work reported here, the most important of these effects of supporting a single-site catalyst on a suitable catalyst support is the replication or templating effect. This means the resulting particle size distribution and morphology of the catalyst support are often mirrored in the particle size distribution and morphology of the resulting polymer particles. This is due to the uniform growth of polymer at the active catalyst sites on and in a catalyst support particle.¹⁶⁸ With sufficient polymer growth in and outside of the catalyst support particles the resulting hydraulic forces break the support particle apart, yielding a polymer particle 20 to 30 times the size of the original catalyst support particle (Figure 24).¹⁶⁹ For an efficient replication, the catalyst support particles need to be fragile enough to break apart during the polymerization but need to be strong enough to avoid breaking prior to the polymerization. A certain amount of porosity is also desirable to ensure catalyst and monomer diffusion into the catalyst support particle to yield uniform polymer growth.¹⁶⁷



Figure 24: Multisite polymer growth typical for heterogeneous catalysts¹⁶⁴

Up to now, research has mainly been dedicated to preventing reactor fouling and to receive particles with no particular control over size and morphology. Most of the produced particles are too large for an efficient PBF process.^{170,171}

3.5 High energy mixing

Mixing processes have the intention to distribute one compound in another compound. This can be achieved by numerous methods with varying complexity. One of the most challenging aspects in mixing is good distribution of nano-compounds in or on polymers. Nano sized compounds tend to form agglomerates, due to their high surface energies. Several high energy mixing devices have been developed to overcome these attractive forces and break such agglomerates. The most common route to achieve a good distribution of nano sized compounds is the application of an ultrasonic treatment in an appropriate solvent.^{172,173} This route has several disadvantages, such as the need of solvent removal and the risk of reagglomeration. A more economical way is the process of high energy dry blending as no drying step and no solvents are required. Employment of a Nara Hybridizer has led to the formation of evenly distributed and immobilized nano sized guest compounds on the surface of host polymer particles. The Nara Hybridizer operates with a centered stator with vertical blades surrounded by a rotor also equipped with vertical blades. Mechanical energy is thus applied to the to be mixed compounds in the form of impact and shearing.^{174,175} Another high energy mixing process, yielding finely distributed nano sized guest particles on the surface of polymer particles, is the dual asymmetric centrifuge.^{176–178} In this process large centrifugal forces are applied to the to be mixed compounds, resulting in high shear rates and inter particle collisions. The basic principle is a mixing container rotating around its central axis while being fixed at an angle on a rotating platform (Figure 25). As this process operates bladeless and the mixing container is easy to clean/change, this process is the most efficient and was employed in this work.



Figure 25: Basic principle of a dual asymmetric centrifuge

3.6 Spray drying

Spray drying is a process to form spherical particles from solution or dispersions. It operates under the basic principle of atomizing a solution or dispersion into a hot gas stream. The high surface area of the produced droplets, combined with the elevated temperatures of the gas, leads to a fast evaporation of the liquid in each droplet, leaving behind a spherical particle.



Air inlet (optional with attached inlet filter)
 Electric heater

- ③ Concentric inlet of the hot air around the spray nozzle
- (4) Spray cylinder
- ③ Cyclone to separate particles from gas stream
- Product collection vessel
- ⑦ Outlet filter
- (a) Aspirator to pump air through system

Figure 26: Schematic diagram of a spray dryer¹⁷⁹

Various particle morphologies can be achieved depending on the process parameters (spraying rate, atomization, gas temperature, concentration, gas pressure/speed) and materials employed (Figure 27).^{180–182}

Dense particles are achieved when the drying rate is as fast as the liquid inside each droplet can be transported to the outside layer. If the drying rate is faster a hard shell is formed leading to hollow particles. If the drying rate is to low the droplet can first form a mushroom- and then a torus-shape, which results in doughnut shaped particles. Raspberry shaped particles or particles with large pores can be formed with the employment of micelle forming surfactants. The focus in this work was to achieve dense spherical silica particles in the low µm range as catalyst support particles.



Figure 27: Various particle morphologies prepared by spray drying¹⁸²

4. Cumulative part of the dissertation

4.1 Toward the Direct Synthesis of HDPE Powders for Powder Bed Fusion Based Additive Manufacturing

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4.1.1 Synopsis and aim of this research

Additive manufacturing (AM), also commonly known as 3D printing, has gained increasing attention in the economical, scientific and everyday world. It describes the process of building a desired part directly from a 3D computer aided design (CAD) model by a layer wise addition of material onto a substrate or on top of itself.¹⁸³ This process operates without the traditionally needed formative or subtractive fabrication and has several advantages, such as freedom of design, mass customization, waste minimization and the possibilities to manufacture complex parts.¹⁸⁴ Additive manufacturing will never supersede mass production of parts as the costs in traditional manufacturing decrease exponentially for every part produced (Figure 28). Nevertheless, it has its justification for the production of highly customized parts (e.g. implants) or small batches (e.g. production of spare parts on demand in the aerospace industry or rapid prototyping).



Number of produced units

Complexity of produced units

Figure 28: Cost of produced parts produced by additive manufacturing and traditional manufacturing plotted against complexity and number of produced units^{10,185,186}

Polymers are by far the most utilized class of materials for AM. Of the different available forms of AM with polymers powder bed fusion (PBF) stands out as it offers the possibilities to generate build parts with high mechanical strength and low anisotropy in the build parts.² But the range of polymeric materials available for PBF is limited to mainly polyamides. This limits the built part properties as well.

Ultra high molecular weight polyethylene (UHMWPE) is a material with an attractive property profile for many applications but the high melt viscosity limits the processability in any procedure. It was tested as candidate for PBF but up to now UHMWPE parts prepared by powder bed fusion do not compare positive to traditional manufactured ones.^{150,152,187,188} The parts often show less mechanical stability as well as dimensional accuracy, e.g. warpage and curling. The aim of this work was the establishment of polymerization techniques leading to advanced HDPE/UHMWPE/dUHMWPE composite powders useful for the preparation of polyethylene based parts manufactured by PBF.

The starting point of this research was to identify a suitable catalyst carrier based on spray dried silica as tailor made catalyst templates for the formation of polymer powders suitable for PBF. In this strategy the first step consisted of the formation of silica micro particles out of dispersed silica by spray drying. The resulting micro templates were subsequently impregnated with a BIP iron (II) catalyst and the polymerization of HDPE started.



Figure 29: Strategy for the formation of polyethylene powders

The goal was to obtain information over activation of the catalyst templates and the subsequent polymerization behavior in regard to the needed PBF-Powder properties (Particle size, morphology and distribution, powder flowability, laser absorption, sinter window (see 3.1.1)) The resulting HDPE powders were tested in a miniaturized PBF setup and the sintering/melting process and adjustment of the process parameters and powder properties was investigated.

The results of these investigations were published in the following publication.

RESEARCH ARTICLE



Toward the Direct Synthesis of HDPE Powders for Powder Bed Fusion Based Additive Manufacturing

Yannick L. Wencke, Friedrich Proes, Philipp Imgrund, and Gerrit A. Luinstra*

Powder bed fusion (PBF) suitable polyethylene particles are targeted by means of a direct synthesis, using a bisimino pyridine iron catalyst (BIP FeCl₂) supported on microsized silica particles. An active support is generated by treating spray dried silica microparticles with a methyl aluminoxane activated BIP FeCl₂ catalyst in toluene. Semibatch ethylene polymerization is mapped with respect to pressure, temperature, and reaction time to find optimal reaction parameters. The optimized synthesis leads to round polyethylene particles with a median size of \approx 50 μ m which have a sinter window of 8–15 °C and an unconfined yield stress (ffc) of 1.5 in a ring shear tester. The Young modulus of injection molded samples is in the range of 150-250 Pa with an elongation at break of about 30%. The powder flowability is improved by coating with nanosilica powder to an ffc of 3.8. Additivitation with carbon black allows to laser sinter the powder to solid parts in a small scale adapted setup for selective laser sintering (PBF/laser beam (LB)/P). Severe caking is preventing the preparation of CAD model conform parts. Commercial HDPE powder for PBF is additivated the same way to give substantially solid built parts, but with similar caking.

1. Introduction

The art of additive manufacturing (AM) with polymer powders is undergoing a renewed and more rapid development and diversification with respect to printing technology and polymeric materials. The scale of expansion can be taken from a subset of also recent reviews.^[1–8] Societal applications of AM in the broadest sense can be identified, at least running inside the sectors of aerospace and automotive, sports, health care, architecture to

The ORCID identification number(s) for the author(s) of this article can be found under https://doi.org/10.1002/mame.202100477 © 2021 The Authors. Macromolecular Materials and Engineering published by Wiley-VCH GmbH. This is an open access article under the terms of the Creative Commons Attribution-NonCommercial-NoDerivs License, which permits use and distribution in any medium, provided the original work is properly cited, the use is non-commercial and no modifications or adaptations are made. that of toys.^[9] The manufacturing and availability of suitable polymeric powders is the decisive factor in the technology, next to and in connection with the print technology.^[4] Today, it seems justified to say that powder bed fusion (PBF) offers the most possibilities to generate built parts with high mechanical strength and low anisotropy in the printed parts, especially also when using fiber composite powders.^[5,8,10]

Powder bed fusion (PBF) processes are based on thin layers of very fine powders, which are spread evenly by a coater on a platform.^[11] The powders are locally fused with a laser beam (PBF/LB) or a binder according to a computer set CAD routine. By lowering the platform and coating again, the next powder layer is created, which after melting in turn is fused with the underlying object. Selective laser sintering SLS (PBF/LB/P) as method of fusion is of particular relevance to the here reported research. SLS melts the powders locally at the surface without completely melting the

particles. The neighboring particle surfaces are welded together mainly governed by the surface tension, capillary forces and melt viscosity. This is usually not as effective as selective laser melting SLM, where a complete melting of the particles is achieved, but may give a better dimensionality (less warping and curling; vide infra) in the built parts.

The requirements on powders for PBF are derived from the overall process and the outcome in terms of built parts. It comprises the constitution and handling of the powder, its thermal and optical properties and the properties of the generated polymer melt (rheology, crystallization) and of the final part (mechanics, dimensions, surface quality).^[11–13]

One key factor in producing a PBF-suitable polymer powder is the flowability of the powder, which profits from round particles with a smooth surface. ^[10,11] Several suitable materials from a thermal view point, cannot be used in a PBF process due to the insufficient flowability and packing density of obtainable powders. Irregular powders suffer in flowability with increased packing density (interlocking).^[14] SLS is carried out inside the sinter window, a temperature range of super cooling between the melting temperature and the onset of crystallization. In an useful PBF powder, the onset of melting upon heating and the onset of crystallization upon cooling are about 20–30 °C apart, like for PA-12.^[10] The short laser irradiation elevates the powder temperature over the melting temperature and the melt

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solidifies by transferring heat to the surrounding particle bed, in the best case initially without crystallization. Subsequent crystallization is then ideally initiated by slow cooling of the whole build chamber leading to evenly distributed crystals in the built part. As a rule of thumb, the printed parts are cooled down in a similar time frame as the building job.^[15]

The crystallization is possibly the most critical part in the PBF process with polymers.^[1,11] Two major build defects can be attributed to inhomogeneous crystallization. The first defect is the immature crystallization of a freshly molten layer of powder called curling. The crystallization leads to a shrinkage of the layer and to stress inside the layer, causing the edges to curl upward.^[16] If the curling is not too severe (e.g., higher than a new layer of powder) the next layer of powder can correct this fault. This building effect leads to a deviation of the built part with respect to the CAD model in z-direction. The second defect occurs later in the building job when inhomogeneous crystallization leads to residual stresses in the complete part, so called warpage. This second defect cannot be corrected and appears after the built job is completed.[16,17] Warpage is a strong disadvantage; preventing it can be achieved to some extent by a controlled cooling rate.^[10,18,19] Additives such as plasticizers can also help to keep the melt viscosity low to allow stress relaxation. Using polymers with a low melt viscosity can help to prevent the build up of stress.

A low viscosity is also beneficial for the welding process itself. When an amount of material becomes molten, an initial "necking" occurs after contacting neighboring entities, leading to bridges of material between the particles and layers. This may result in in porous built parts.^[11,20] The extension of melting the particle surface and subsequent flow together with the particle packing density determines the overall outcome of the sintering. The final material properties are also determined by the several stages of the material relaxing after the solidification. Built parts from polymer powders along SLS (PBF/LB/P) often lack the inherent strength of the parent polymers.^[11]

The post-synthesis production of (commodity) polymers into PBF suitable powders constitutes an additional production step in need of specific technologies and further development. Standard polymers are shaped into a narrow range of particle sizes and optionally an additivation is carried out to adjust the optical properties for absorbing laser light, powder flow properties and melt viscosity. PBF suitable powders best have a size with a median in the range of 60 µm and a narrow particle size distribution.^[1,11] The major polymers used in PBF in the context of SLS are polyamides (PA-12), but also reports on PEK, PEEK, PCL and even polyethylene (HDPE) or polypropylene can be found.^[4,6] These examples are specifically used in SLS.

Current commercial offered powders are the result of a dedicated post synthesis production process, all with their specific requirements and outcome. Cryogenic milling gives jagged and uneven particle morphologies with a broader particle size distribution. Particle edges may be rounded for a better flowability by hot gas, and a sieving process may be implemented to reduce the particle size distribution.^[21,22] Precipitation of powders from solutions is effective and mainly used for polyamide PBF powders.^[23] Coextrusion of two immiscible polymers and subsequent dissolution of the unwanted component can lead to suitable sized and shaped powders as well.^[24] Several other techniques for the pro-



duction of PBF powders with a need of more or less elaborate equipment are used too, like spray drying^[25,26] (from conventional solvents as well as from polymer melts solvatised in supercritical gases),^[27] wet grinding^[28] and fiber cutting.^[29]

Perfect round and smooth surfaced PBF powders could also be prepared in direct polymerization processes. Morphology control can be reached in emulsion or suspension polymerizations in water, but also in gasphase polymerizations[30] or precipitation polymerizations on a supported catalyst in slurry.[5] Latter is common practice in the preparation of polyolefins.[31-33] The current technologies for preparing polyolefin particles are optimized for other purposes and the products are mostly not directly suitable as PBF powders on account of their larger size. The supported gasphase or slurry polymerization of ethylene and propylene offers the possibility of reaching control over the morphology.^[31] Control over the action of homogeneous catalysts was targeted for the preparation of polyolefins with enhanced property profiles. These efforts aim at the reduction of the severe reactor fouling observed for homogeneous olefin polymerization, and to increase the bulk density of the resulting polymer.[34]

We set out to directly prepare polyethylene powders (PE) useful in PBF applications by the replication of catalyst particle morphology in a slurry polymerization, i.e., target is to produce particles in the size range below 200 µm, with a sufficient powder flowability, a sufficient sinter window and acceptable laser light absorption (printability triad).^[11] In contrast to the current polyolefin manufacturing technology of having a fragmenting catalyst particle, leading to the "raspberry" morphology of the commercial products, an integer support was chosen as a carrier for the catalyst.[31,32,35-39]A mixture of such supports would also give access to well-distributed particle size distributions, which can help somewhat to increase the density of the built parts. It was also the intention to extend the availability of materials for PBF into the realm of commodity polymers such as HDPE,[17,40-42] the main objective of larger research effort (vide infra). A consideration of the societal use of polyolefins, may lead to the conclusion that polyethylene is always of particular attractiveness, i.e., would also be for PBF: it is cost efficient in its synthesis and easy to recycle.^[5,17,43] At least one commercial source of high density HDPE powders for PBF is available.^[44] The product is prepared by post-synthesis procedures. Procedures including the sieving of primary particles were described.[42]

An optimization of polyethylene powders for the purpose of PBF seems also appropriate in lieu of the few reports of the use of HDPE in that context. Following on an early study, little new results were subsequently reported on the PBF of $\mathrm{HDPE}^{[45,46]}$ It was described that (only) porous built part are the result. The larger particles gave PBF materials with lower porosity, but with inferior material properties as the consequence of necking. A more recent report, readdressing the matter, concludes that parts can be obtained but also that the mechanical integrity needs improvement.^[47] The direct preparation of PBF suitable polyethylene powders would offer the possibility to tune the thermal and rheological properties of the matrix polymer. This is very much of importance to the built part properties. The direct preparation of suitable PE powders would make the elaborate generation (i.e., grinding, thermal rounding, sieving) of powders obsolete, have the additional advantage of tailoring the polymer molecular weight and its distribution and give the possibility to

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perform an in-situ additivation for the purpose of laser light absorption or adjusted mechanical properties.^[5]

The catalyst used in this orientating study was derived from N,N'-(2,6-pyridinediyldiethylidyne) bis[2,6-diethyl-benzenamine iron dichloride **1**. It produces broad distributed polyethylenes in the range of 10–100 kDa that thus have properties in the transition of waxes to tough materials with a relatively low melt viscosity^[48,49] The focus is on the preparation of processable and sinterable powders. The final material properties are of secondary importance and could be tuned using other derivatives or mixtures of bisimine pyridine iron catalyst family in a follow up study.^[43]

2. HDPE Templating from Silica Microspheres

Although the current technology of preparing PE powders is not directed toward the preparation of dense particles in a size between about 30 and $\approx 150 \mu$ m, an adoption could bring this easily about. The incorporation of additives in the process would also be possible within certain limits of compatibility to the catalytic system for ethylene polymerization. Also nanofibers could be incorporated, an approach that could lead to enhanced material property profiles.^[6] Most commonly used materials for catalyst supports are inorganic materials, such as silica-, alumina- or magnesium dichloride-particles.^[37] Silica particles were chosen as support.^[34] They are available in a range of densities and sizes. Silica is a good absorber for IR laser radiation^[48] and a composite of PE/silica will have acceptable material properties.^[49] It has also been pointed out, that a composite also may improve mechanical performance in fused filament fabrication.^[50]

Preliminary experiments were carried out to identify suitable types of silica microparticle supports. The fixation of the catalyst on the support can either be performed by a physical absorption, electrostatic interaction or a chemical reaction.^[51] The interaction between catalyst support and catalyst can be complex and lead to a plethora of different effects. The catalyst system selected for the ethylene polymerization is based on bisimine pyridine iron dichlorides.^[52–54] Heterogenizing BIP catalysts usually leads to higher productivities.^[55] These type of complexes are easy to prepare and handled and give, in combination with aluminum alkyl cocatalysts, highly productive polymerization catalysts. A tuning of the polyethylenes properties would be feasible by variation of the ligand structure, and the derived technology would allow a fast adaption by variation of the complex.

One commercial candidate for silica support was colloidal silica Ludox-Cl. It was isolated from water by spray drying. Cores of massive and hollow silica microspheres could easily be identified in optical microscopy. Reacting the spray dried silica with methyl aluminoxane (MAO) or triethyl aluminum (TEA) gives an activating support after isolation and suspension in toluene. Ethylene polymerization was initiated by adding the iron complex as toluene suspension to the MAO activating support, also suspended in toluene. It was carried out at constant pressure, resupplying any ethylene that had reacted (semibatch mode). Severe reactor fouling was found in these experiments. The BIP FeCl₂ complex 1 was activated for ethylene polymerization after its addition, but was not effectively retained at the particle. The preparation of an activating support by reaction of aluminum alkyls with maiden silica (not dried) was also established. Using this type of treatment for activating the support in combination with 1 yielded a HDPE/silica composite, however with some agglomerated particles and amorphous polyethylene.

More suitable results were obtained along an adapted method of incipient wetness for reaching an active polymerization system.^[56] An amount of methyl aluminoxane (MAO) in toluene was mixed with 1 and subsequently applied to the dried silica microparticles. The solvent was removed to give an active supported catalyst. Polymerization of ethylene on these particles was achieved in toluene containing triethyl aluminum (TEA) at a concentration of 9 mmol L⁻¹. TEA acts as a scavenger and deactivates 1 for polyethylene formation (by complexation and chain transfer) at these concentrations, thus any leakage of active catalyst from the support results in an effective quenching of polymerization activity. This method and effect was described before in zirconocene mediated ethylene polymerization.^[57]

The polymerization using the adapted incipient wetness method and spray dried colloidal silica microparticles yielded silica/polyethylene core-shell particles. The silica microparticles were not fragmented during the polymerization process. The resulting composite particles were in the range of $\approx 30 \,\mu\text{m}$ when using core particles in the range of $\approx 10 \,\mu\text{m}$ after 60 min of polymerization. A closer examination shows that the surface is quite rough with single polymer particles/lamellae sticking out of the surface. In addition, the particles show evidence of polymer broken away from the silica surface, in part exposing the silica core again. Longer reaction times led to even more delamination of polyethylene from the surface of the silica core, unfavorably leading to irregular particles and some debris (**Figure 1**; Figure S1, Supporting Information).

Prior coating of the Ludox-Cl silica microparticles with tetraethoxy silane TEOS led to an increased dispersibility in toluene and a slightly increased polyethylene adhesion to the surface of the silica particles.^[58] No increased particulate growth or templating effect of the particles could be observed. Also using a similar trimethyl amine stabilized colloidial silica variant, Ludox-TMA, as basis for the spray dried microparticles did not lead to an improvement in catalyst template replication, core-shell adhesion or increasing particulate growth. This behavior seems thus related to the mobility of the catalyst close to support surface, and the constitution of the silica. The chosen combination of polymerization reaction, support, cocatalyst and catalyst was not ideal for the purpose.

Thus, another support basis was considered in form of precipitated silica Perkasil 300 KS. Dispersion in water and a subsequent spray drying process led to small agglomerates of single round particles. The above-mentioned incipient wetness treatment with MAO/catalyst solution was also applied to turn the silica into an active supported catalyst particle. PE formation could be induced by addition of a suspension to a reactor filled with an ethylene saturated toluene solution containing TEA. Again, the catalyst system was immediately active as ethylene was consumed from the start and the particles grew in size.

A significant increase in particle size occurs to a median of $43 \ \mu\text{m}$ in the first 60 min of polymerization. Light microscopic images of polyethylene particles periodically taken from the reactor indicate the increase in particle size and with substantial round morphologies (**Figure 2**). A minor broadening of the overall particle diameter distribution along with a shift toward larger



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Figure 1. SEM micrographs of polymer particles with visible silica cores out of spray dried Ludox-Cl colloidal silica. A) Overview over the resulting polymer particles. B) Delaminated cores shell particles. C) Surface of polymer particle. D) Shattered remains of a core shell particle, laminar polymer strands, no strong connectivity among PE, PE, and support.



Figure 2. Polyethylene microparticles at various stages during a polyreaction. A) 15 min, B) 30 min, C) 45 min, D) 60 min. Reaction conditions: 4.8 μmol 1 with 0.72 mmol MAO on 1 g of Perkasil 300 KS, 5.4 mmol TEA, 20 °C, 3 bar ethylene, 200 RPM, 600 mL toluene, 60 min.



Figure 3. Yield and silica content of polymer particles from 1 heterogenized on spray dried Perkasil 300 KS (left) and the resulting particle size distributions (right). Reaction conditions: 4.8 µmol 1 with 0.72 mmol MAO on 1 g of silica microparticles, 20 °C, 3 bar of ethylene pressure, 200 RPM, 600 mL of toluene. 5.4 mmol TEA. Data at 120 min reaction time was at half the amount of active support.

0

100 125 150 175 200 225

time [min]

particles sizes is found with advancing reaction time (Figure 3). The (median) particle size increases further at a much slower pace to 90 μ m at 180 min of polymerization time.

75

50

0

ò

25

The morphology of the template was substantially copied, and the original distribution of silica particles resulted in a comparable distribution of HDPE@silica core-shell particles. Most notably, the surface of the received particles smoothens with ongoing reaction time (**Figure 4**), giving the most smooth surface after 180 min of reaction time. However, this also leads to a substantial fraction of particles larger than 200 µm, which is unfavorable for PBF applications (Figure 3). Reaction times longer than 60 min were thus not suitable for the set target of this work. Longer reaction times also seems to result in the formation of "fines", the surface is partially covered with smaller protuberances.^[32] Fines negatively influences the flowability.

SEM images of the product after 60 min of polymerization time give a similar impression as the light microscopic analysis (Figures 2 and 4). The individual particles appear round, but overall the images also indicate a partial association. This may represent an intermediate stage of the process of HDPE@silica particle formation and separation.^[59] The original close contacts between the silica particles are released as the polymer shell grows, pushing the cores away from each other. A reaction at 0.5 bars of ethylene pressure with lower ethylene consumption rates gives a glance at the early phase of particle separation. Pseudo agglomerated smaller particles are recognizable in SEM images (Figure 5), and a bimodal distribution is detected in DLS measurements (Figure 6).[32] The breaking up of such agglomerates may also lead to the ripped particles found when using Ludox-Cl colloidal silica, i.e., when polyethylene shells are more strongly connected to each other and not so much to the silica cores (Figure 1). Alternatively, this may also be the result of partial catalyst leaching, forming the polymer away from the surface.

Higher ethylene pressures lead to an increased yield but comparable particles after 60 min, with some experimental spread with respect to size (Figure 6). This is in accordance with the view that initially the HDPE shell is formed on all silica particles, separating them, followed by a much slower consecutive growth on account of arising ethylene diffusion barriers through the shell.^[60]

Lowering of the catalyst loadings at the support was not useful for obtaining more separated particles. It led to lower yields of polyethylene and broader distributions (Figure S2, Supporting Information). The absorption of the catalyst at the surface is most probably a fast and irreversible reaction and ideal mixing of solution and particles is apparently not achieved. Lower precatalyst loadings also lead to less dense polymer shells that also are more fragile. Broken and deformed particles are visible in SEM analysis (Figure S3, Supporting Information). Higher catalyst amounts (4.8 μ mol) are therefore more favorable for obtaining robust particles. Increasing the reaction temperature while leaving the catalyst concentration constant gives a higher yield and a more smooth, dense shell (**Figure 7**). The increase in smoothness and yield again went along with a resulting particle size exceeding the 200 μ m boundaries for efficient PBF action.

100

Particle diameter [µm]

1000

Another factor influencing the formation of single particles was the amount of ethylene available for the activated catalyst particles at the onset of reaction. The polymerization is generally initiated by adding the catalyst to an ethylene saturated toluene solution. Experiments without the initial saturation led to a broader particle size distribution and smaller particles. Reaching an immediate adequate mixing after fast dosing of the active catalyst support is also essential to the outcome. A slower, gradual dosing of the support leads to a bimodal particle size distribution. Beside toluene, heptane was also used as reaction medium. This gives similar results, however, comes along with a broadening of the distribution with also larger particles present, and is not preferred. These results indicate that when starting with the silica particles in the range of 5 µm, smooth and dense particles will partly exceed the 200 µm boundary, irrespective of polymerization conditions and catalyst loadings. Therefore, the local optimum for directly obtaining HDPE@silica with an acceptable profile for a PBF application was a polymerization for 60 min at 20 °C. This is the best solution within the constraints of this study using BIP iron catalyst 1, its concentration and the resilient silica particles in the range of 5 µm.

The isolation of the particles from the reactor also needs a procedure preventing an agglomeration of the swollen polyethylene particles. A convenient procedure is a change in solvent polarity by diluting the toluene with ethanol after the reaction. This solvent exchange resulted in a uniform and redispersable distribution. Direct filtration of the reaction slurry led to a cake that could not simply be broken up to individual particles again, giving evidence for some particle agglomeration (Figure S4,



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Figure 4. SEM micrographs of polyethylene synthesized with 1 heterogenized on spray dried Perkasil 300 KS at reaction times of A) 60 min, B) 120 min, C) 180 min. Reaction conditions: 4.8 µmol 1 with 0.72 mmol MAO on 1 g of support, 5.4 mmol TEA, 20 °C, 3 bar ethylene, 200 RPM, 600 mL toluene, 60–180 min.



Figure 5. SEM micrographs of polyethylene synthesized with 1 heterogenized on spray dried Perkasil 300 KS at 0.5 bars of ethylene. Reaction conditions: 4.8 μmol 1 with 0.72 mmol MAO on 1 g of support, 20 °C, 5.4 mmol TEA, 200 RPM, 600 mL of toluene, 60 min.



Figure 6. Yield and silica content in semibatch reactions at various reaction pressures with **1** heterogenized on 1 g of heterogenized on spray dried Perkasil 300 KS (left) and the resulting particle size distributions (right). Reaction conditions: 4.8 µmol **1** with 0.72 mmol MAO on 1 g of support, 20 °C, 5.4 mmol TEA, 60 min, 200 RPM, 600 mL of toluene.

time [min]



Figure 7. SEM micrographs of polyethylene synthesized with 1 heterogenized on spray-dried Perkasil 300 KS at 40 °C. Reaction conditions: 4.8 µmol 1 with 0.72 mmol MAO on 1 g of spray dried silica micro-particles, 3 bar ethylene, 200 RPM, 600 mL toluene, 5.4 mmol TEA, 60 min.

Supporting Information). Ultrasonic treatment of the polymer particles could also not fully restore the original single particle distribution.

3. Mechanical Properties of Bulk Material

The mechanical property profile of the composites obtained from Perkasil 300 KS as catalyst support generating the polyethylene shell at 20 °C at 3 bars of ethylene pressure was determined on injection molded samples (Figure S5, Supporting Information). The shore hardness D increases from 70.6 \pm 1.3 to 78.4 \pm 0.5 already at the low content of 1.6 wt% silica. The presence of more silica did not increase the hardness any further, as would be expected for the core-shell constitution with an effectively dispersed filler. The hardness more or less results from the polyethylene crystals.^[48,49] The Young modulus was in the low range of 244 \pm 16 MPa at 0 wt% silica reaching to 154 \pm 8 MPa at the highest silica content of 11 wt% (smallest shell). This indicates that the molecular weight is in the lower range for the action of catalyst 1.[61] A molecular weight determination by size exclusion chromatography was hampered by the presence of the silica particles. The elongation at break decreased from 33.2 \pm 9.6 % at 0 wt% silica to as low as $15 \pm 0.8\%$ at 7.5 wt% silica. This is expected for a higher filled composite with a fine, even filler distribution. The ultimate tensile stress is not affected by the silica content apart from the sample with a silica content of 11.5 wt% where the ultimate tensile stress increases from average of 33 ± 3.4 MPa to 42.2 ± 1.7 MPa (mol. mass effect). Samples show a clean, even break surface after cryo-fracturing (Figures S6–S8, Supporting Information). A few single silica micro particles in the $\approx 10 \ \mu m$ range were detected, no significant agglomerations of silica were found, consistent with the expectation of single particles. The analysis of the surface with the highest loading (smallest shell) shows that the silica micro particles are distributed across the whole break surface. These results indicate that the silica particles are more or less unchanged after the polymerization and subsequent processing.

Particle diameter [µm]

4. PBF Suitability

The sinter window was determined between the first onset of melting in DSC measurements and the first onset of crystallization. As silica can act as a crystallization aid, the thermal properties may differ from that of neat polyethylene with the same mass and mass distribution.^[62] The determined sinter windows, the region of super cooling between the melting of the maiden material and subsequent crystallization, are small (14.8–8.7 °C; **Figure 8**) compared to the sinter window of commercial PA12

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Figure 8. DSC of maiden HDPE@silica (2 wt%) and HX 11 with indicated sinter windows.

PBF powder (up to 32.4 °C^[63,64]). This represents a challenge for the homogenous temperature control in the building chamber of a PBF machine. Temperature differences inside the building chamber can easily lead to inhomogeneous building conditions (local crystallization) and subsequently to inferior built parts (warping, curling).^[65] However, the range is still appreciably larger than commercial HDPE HX 11 powder for laser sintering by Diamond Plastics of less than 4 °C. The melting enthalpy of maiden HDPE@silica is in the range of 195 J g⁻¹ a high value in comparison to the value of about 55 Kj mol⁻¹ found for the thermally processed commercial HDPE powder and also for thermally equilibrated HDPE@silica. A high enthalpy of melting is favorable for diminishing caking that results from melting of particle surface outside the laser scanning region by scattering.^[66] Caking, the adhesion of particles to the built part, may also be reduced by the addition of IR absorbers, like carbon black (CB).

Particle flow property data were gathered in measurements with a ring shear tester, which at least gives an indication on the flow behavior in a recoater.[11,67] The obtained ratio between the consolidation stress and the unconfined yield stress (ffc) serves as numerical value for the comparison of flowability between the various powders. An ffc value of 1 indicates limited flowability, while a ffc number of 10 or higher indicates a free-flowing powder.[63] The ffc values of the obtained HDPE@silica powders between 1 and 2 indicate that a preprocessing in terms of increasing flowability before PBF testing is prudent (Table 1). The flowability of the maiden silica templated HDPE particles also lie below that of commercial HDPE particles. This must not surprise as latter powder is optimized for the purpose. The bulk density of the HDPE@silica particle powder was only 175 kg m⁻³ compared to 403 kg m⁻³ for the commercial HDPE powder, also indicating that a further densification would be necessary. The optimal polymerization conditions with regard to size led to these and further limitations (vide infra).

A compacting in a dual asymmetric centrifuge as a method of high energy impacting was carried out to obtain a powder with a higher bulk density and ffc value. The received higher ffc value



Table 1. Flow function, bulk density, and sphericity of silica templated HDPE and commercial HDPE HX.

		HDPE HX			Silica templated HDPE			
	ffc 500 Pa	Bulk density (kg m ⁻³)	Sphericity	ffc 500 Pa	Bulk density (kg m ⁻³)	Sphericity		
naiden	3.09	403	0.77	1.73	175	0.46		
HE mixing ^{a)}	1.51	409	0.81	2.79	239	0.85		
v/additives ^{b)}	3.12	447	0.84	3.82	253	0.74		

^{a)} High energy mixing; ^{b)} Additivation with 1 wt% of silica powder and 0.25 wt% of carbon black.

goes along with a higher sphericity, reaching the level of commercial HDPE PBF powder. The reshaping/deagglomeration through physical impact is also indicative of the less dense powder packing from the synthesis procedure (polymerization and work-up). The rather low sphericity of 0.46 of the maiden powder is easy to relate to the particle-on-particle situation found in SEM images of products after 60 min (Figures 2 and 4). Surprisingly, the impact of the high energy mixing severely degraded the ffc value of commercial HDPE. This might be due to the not perfectly spherical and rougher particles of the product, interlocking in the mixing process, and/or the formation of fines, inhibiting flow (Figure S9, Supporting Information).^[11]

The low ffc values of the particles obtained after high energy impact led to the decision to add nanosilica as a flow aid. This was limited to 1 wt%, enough silica to enable efficient recoating without substantially changing the mechanical properties of the resulting part. Polyethylene is almost transparent to the wavelength (10.6 µm) of the used infrared laser.^[68] The absorption of laser light was inflicted by the additivation with 0.25 wt% of carbon black (CB). This choice was for safety reason in our facilities, precluding the use of the more effective carbon nanotubes. Latter compounds could also create superior electric conducting materials.

The addition of the chosen amount of silica as flow agent and CB as laser light absorption additive led to a further increase of the flowability, giving an ffc value of 3.82 for the synthesized particles.^[69] The addition of the optimized amount of silica and CB restored the flowability of the commercial HDPE to its former value and increased the bulk density and the sphericity. Thus, two types of powders were made available with reasonable properties for PBF/LB/P testing.

The powders were tested in an adapted PBF equipment of the EOS company (EOS P390). An insert that reduced the build volume allowed to use smaller amounts of powders, a prerequisite for fast testing of experimental powders.^[70] The shape of the built parts should match the previously selected CAD-file as close as possible.^[71] The PBF building process with silica templated HDPE powder with 1 wt% of silica and 0.25 wt% of CB were executed with an empirically found best practice parameter set. The layer thickness for the recoater operation was increased to 240 µm from the 120 µm for PA12 particles with a median particle size of 60 µm. This was done to accommodate for the larger particles in the received particle size distribution. The standard layer thickness of 120 µm was used to sinter HDPE HX 11.



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Figure 9. Set of tensile test specimens of the DIN type 1bb of HDPE (HDPE HX 11, Diamond Plastics) with the addition of 1 wt% of nanosilica and 0.25 wt% of CB build by PBF with the current best practice parameters.



Figure 11. Set of tensile test specimen of the DIN type 1bb of silica templated HDPE with the addition of 1 wt% of nanosilica and 0.25 wt% of CB build by PBF with the best practice parameters.

Of high interest in this preliminary study was the relative performance of the directly prepared particle to the commercial offered HDPE PBF powder. The PBF building process with it, i.e., also additivated with 1 wt% of silica and 0.25 wt% of CB could be executed with the best practice parameter set without any warping or curling disturbing the build job (**Figure 9**). The built tensile test specimens were enclosed by a large amount of adhered/sintered powder, which also made separation of tensile test specimens without damaging impossible. The break surface, however, exhibited a very clean and even break with almost no pores and no remnants of silica visible. The built part is one solid part without any faulty inter layer sintering or neck sintered particles. Outside of the laser track adhered particles were still very prominent leading to the earlier observed massive caking (Figure 10). This is presumably due to scattered laser energy penetrating the transparent polyethylene powder bed and causing minor sintering/caking outside of the laser irradiated path. A laser power of 36 W was used, lowering the power to, e.g., 12 W did not lead an adequately melting of the particle surface.^[72]

The built part from the silica templated HDPE particle showed less caking (**Figure 11**). However, a separation of the built tensile test specimens was also not possible. The lower powder density leads to a distinct porosity in the laser irradiated areas (**Figure 12**). SEM imaging revealed mainly neck sintered and next to partially molten particles. This result may be related to the low inherent density of the powder particles, leading to incomplete consolidation after the laser irradiation.



Figure 10. SEM micrographs of the cryo-fractured tensile test specimens and its top surface of commercial HDPE (HDPE HX11, Diamond Plastics) with 1 wt% of nanosilica and 0.25 wt% of CB built by PBF.

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Figure 12. SEM micrographs of the cryo-fractured tensile test specimens of silica templated HDPE with 1 wt% of nanosilica and 0.25 wt% of CB built by PBF.

5. Conclusions

Templated HDPE particles with suitable sizes for PBF/LB AM were prepared in a scalable and versatile method using spray dried microparticles of commercial precipitated silica as template and a BIP FeCl₂ complex as precatalyst. The formation of substantial single, spherical particles with a suitable size is possible, however, until now with a low (inherent) density. The size sets a limit to the obtainable density of the particles. The support, supporting method, polymerization conditions and workup procedure are factors that influence the outcome in terms of powder properties and thus can be used for a further optimization. The data show that templating HDPE particles from spray dried precipitated silica and subsequent mixing those polymeric particles with silica and CB generated powders with acceptable flowability and acceptable roundness, in the same ballpark as commercial HDPE PBF powder (albeit with a half of the lower bulk density). Initial PBF suitability was proven with mixed results regarding the built parts. Solid built parts were obtained, but at the cost of a severe caking.

A dedicated development of powder preparation and laser sinter protocol has the potential to make HDPE a useful PBF material. Optimizations are necessary with respect to the sintering parameters (less caking by scattered laser rays) but also with respect to the molecular weight /distribution (lower molecular weight leading to better melt flowability and less neck sintering). The templated particles are rather porous after the synthesis, and an optimization potential is obviously present. Current research is directed toward in-situ additivitated PE particles with a higher powder density and better powder flowability, and starting from smaller and more narrow distributed silica particles.

6. Experimental Section

Spray Drying of Precursor Silicas: Spray drying was performed on a Minispray Dryer 290 with an inert loop B-295 of the company Büchi. The colloidal silica dispersions were diluted to preference and used directly. In experiments with precipitated silica Perkasil 300 KS, the silica was firstly dispersed by ultrasound. Typically 22.5 g of Perkasil were added to 277.5 mL of deionized water. The dispersion was subjected to 3 times 10 min ultrasound with a Sonopuls 2070 of the company Bandelin equipped with a V70T Sonotrode head at 80 % amplitude. The subsequent spray drying was executed with the aspirator at 80%, the pump at 40% and the pressurized air at 30%. The inlet temperature was 180 $^\circ C$ and the outlet temperature 77 $^\circ C.$

Synthesis Procedure for the Silica Templated HDPE Particles: In a Schlenk-vial 1 g of spray dried silica was dried in vacuo at 150 °C for 2.5 h. Subsequently, in an evacuated Schlenk-vial the desired amounts of precatalyst 1, MAO and dry toluene were added (typically 2 mL of 2.4 $\mu mol.mL^{-1}$ of 1, 0.42 mL of MAO, 3.5 mL of toluene). The activated catalyst solution was then transferred to the dried silica using a syringe. The silica and catalyst solution were mixed using a laboratory mixer and dried in a dynamic vacuum until a free-flowing beige powder was received. The dried silica was dispersed in 6 ml of dry toluene and injected into the prepared reactor. The polymerization set in immediately. Ethylene consumption was monitored, a massflow controller kept the pressure at the preset value. After the desired reaction time, the excess ethylene was discharged, and the reaction was quenched by the addition of small aliquots (5-20 mL) of ethanol. The resulting slurry was then mixed with \approx 1.5 L of ethanol and filtered. The white powder was collected on a filter frit and dried in a vacuum oven at 40 °C overnight. The silica content was calculated from the yield of the isolated polymer and the amount of silica particles used in the synthesis, assuming a complete incorporation into the product.

Additivation of Polyethylene Particles: The commercially obtained and the synthesized polyethylene particles were independently mixed with carbon black Ketjenblack EC 300J (Weber und Schaer, Hamburg, Hamburg, Germany) and additionally with silicon dioxide nanoparticles (Ionic Liquids Technologies GmbH, Heilbronn, Baden-Württemberg, Germany). Mixing was performed separately for each additive, using a Speedmixer DAC 400 (Hauschild & Co KG, Hamm, North Rhine-Westphalia, Germany), switching between a cooling step, where the mixing container is cooled with ice water, and a mixing step with 2500 rpm for one minute, for a total of five cycles for each additive.

Adapted EOS P390 for PBF Testing: To accommodate efficient testing a reduced building chamber, housed inside a commercial PBF machine (EOS P390), was designed and built. The reduced building chamber has been built in close cooperation with/at the Fraunhofer IAPT. Several issues were addressed such as correlating the setpoint temperature and the actual temperature on the powder surface, adjusting the gap distance between parts so no powder leakages occur and insulating/heating the build chamber. The optimization strategy of the PBF process was executed as follows: The starting temperature was chosen at the low end (120 °C) of the sintering window and efficient recoating was tested for several layers at the chosen temperature after the machine reached a thermal equilibrium. Subsequently, the first laser light exposures were tested with a low laser power setting. Ideally, the lowest amount of laser energy is needed to sufficiently melt the material. This minimizes the risk of melting outside of the wanted geometry, as well as minimizing the risk of burning the material. The resulting exposed powder was evaluated for warping or curling. If no dimensional deviation was observed and the recoating process could

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continue without any disturbances the build job was finished. The built parts were then manually checked for mechanical stability. This process was repeated until a set of parameters was reached where the polymer in the laser track is consolidated and dimensionally stable. Empirical found best practice parameters were: Laser Power 36 W; Layer thickness 0.24 mm; Scanspeed 1500 mm.s⁻¹; scanline distance 0.3 mm; Energy density 1.33 J mm⁻³; Exposure speed mm² s⁻¹; single exposure.

DSC Measurements: Melting and crystallization of the polymer composites was investigated using a DSC1 of the company Mettler Toledo (Columbus, Ohio, United States). Standard non-isothermal crystallization experiments were executed for all sample compositions in which each sample was heated from 25 to 250 °C at a heating rate of 10 K min⁻¹. The sample was held at 250 °C for 5 min and then cooled to 25 °C with a cooling rate of 10 K min⁻¹. After holding the sample at this temperature, the sample was subjected to a second heating and cooling cycle with the same parameters as above. All experiments were executed under a nitrogen atmosphere.

Particle Size, Distribution, and Shape: Particle size and distribution of the polymer powders and composites were measured on a HELOS KR laser diffraction sensor equipped with a RODOS/GRADIS dry dispersion setup of the company Sympatec (Clausthal-Zellerfeld, Lower Saxony, Germany). Particle roundness was determined by a dynamic image analysis according to ISO 13322-2 with a Camsizer XT of the company Retsch. (Haan, North-Rhine-Westfalia, Germany)

Mechanical Measurements: Tensile test specimens of the type 5A (DIN EN ISO 527) were prepared by injection molding at 180 °C with 750 bars of pressure with a HAAKE Minijet II of the company Thermo Fischer Scientific (Waltham, Massachusetts, United states of America). Tensile testing was performed subsequently on a Zwicki-Line Z1.0 of the company ZwickRoell (Ulm, Baden-Württemberg, Germany) with 1 kN force transducer and a crosshead speed of 50 mm min⁻¹. Samples were kept at room temperature and under the exclusion of moisture prior to measurement.

Imaging—SEM: Samples were coated with carbon using a Leica ACE 600 prior to analysis with a LEO 1525 Gemini scanning electron microscope (both: Wetzlar, Hesse, Germany). Micrographs were recorded with an acceleration voltage of 5 kV. Optical microscopy was performed on a DMi8 microscope of the company Leica.

Powder Rheology: Powder flowabillity measurements were executed on a ring-shear-tester RST-XS.s of the company Dietmar Schulze (Wolfenbüttel, Lower Saxony, Germany). A sample of 20 g was placed inside the ring shear tester and subjected to a pressure of 500 Pa. Measurements were subsequently in 75 Pa intervals down to 200 Pa.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

Research data are not shared.

Keywords

additive manufacturing, ethylene polymerization, morphology control, powder bed fusion, silica supported catalysis

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- [1] J.-P. Kruth, G. Levy, F. Klocke, T. Childs, CIRP Ann. 2007, 56, 730.
- [2] L. J. Tan, W. Zhu, K. Zhou, Adv. Funct. Mater. 2020, 30, 2003062.
- [3] T. D. Ngo, A. Kashani, G. Imbalzano, K. T. Q. Nguyen, D. Hui, Composites, Part B 2018, 143, 172.
- [4] A. Wegner, Phys. Procedia 2016, 83, 1003.
- [5] S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Chem. Rev. 2017, 117, 10212.
- [6] P. Parandoush, D. Lin, Compos. Struct. 2017, 182, 36.
- [7] X. Wang, M. Jiang, Z. Zhou, J. Gou, D. Hui, Composites, Part B 2017, 110, 442.
- [8] J. Saroia, Y. Wang, Q. Wei, M. Lei, X. Li, Y. Guo, K. Zhang, Int. J. Adv. Manuf. Technol. 2020, 106, 1695.
- [9] B. Berman, Bus. Horiz. 2012, 55, 155.
- [10] M. Schmid, Laser Sintering with Plastics: Technology, Processes, and Materials, Carl Hanser Verlag, Munich 2018.
- [11] C. A. Chatham, T. E. Long, C. B. Williams, Prog. Polym. Sci. 2019, 93, 68.
- [12] A. Gebhardt, Additive Fertigungsverfahren: Additive Manufacturing und 3D-Drucken für Prototyping – Tooling – Produktion, 5th ed., Hanser, München 2016.
- [13] B. Utela, D. Storti, R. Anderson, M. Ganter, J. Manuf. Processes 2008, 10, 96.
- [14] D. Drummer, M. Drexler, F. Kühnlein, Phys. Procedia 2012, 39, 500.
- [15] M. Zhao, K. Wudy, D. Drummer, Polymers 2018, 10, 168.
- [16] C. Nelson, Proc. Solid Freeform Fabr. Symp. 1995, 159.
- [17] M. Schmid, A. Amado, K. Wegener, J. Mater. Res. 2014, 29, 1824.
- [18] P. Forderhase, M. Ganninger, K. McAlea Proc. of the 4th European Conf. on Rapid Prototyping and Manufacturing, Nottingham, Belgirate, Italy 1995.
- [19] P. Forderhase, M. McAlea, M. Michalewicz, M. Ganninger, K. Firestone, Solid Free. Fabr. Symp. Proc. 1994, 102, 102.
- [20] C. T. Bellehumeur, M. Kontopoulou, J. Vlachopoulos, *Rheol. Acta* 1998, 37, 270.
- [21] P. Hejmady, L. C. van Breemen, P. D. Anderson, R. Cardinaels, Powder Technol. 2021, 388, 401.
- [22] S. Xi, P. Zhang, Y. Huang, M. Kong, Q. Yang, G. Li, *Polymer* 2020, 186, 122044.
- [23] M. A. Dechet, J. Schmidt, Proc. CIRP 2020, 94, 95.
- [24] D. Drummer, M. Medina-Hernández, M. Drexler, K. Wudy, Proc. Eng. 2015, 102, 1918.
- [25] A. B. D. Nandiyanto, K. Okuyama, Adv. Powder Technol. 2011, 22, 1.
- [26] M. S. Wahab, K. W. Dalgarno, R. F. Cochrane, S. H. Member, Lect. Notes Eng. Comput. Sci. 2009, 1499.
- [27] C. Eloo, M. Rechberger, Neue Technologien zur Herstellung thermoplastischer Pulver, in *Produktgestaltung in der Partikeltechnologie*, Fraunhofer Verl, Stuttgart 2011, p. 353 ff.
- [28] J. Schmidt, M. Sachs, C. Blümel, B. Winzer, F. Toni, K.-E. Wirth, W. Peukert, Proc. Eng. 2015, 102, 550.
- [29] J. Wulfhorst, G. Seide, T. Gries, D. Rietzel, D. Drummer 11th World Textile Conf. AUTEX (11th World Textile Conf. AUTEX, Mulhouse), Autex, Mülhouse, France 2011.
- [30] K. Franke, H.-U. Moritz, W. Pauer, Chem. Ing. Tech. 2017, 89, 490.
- [31] R. Hoff, Handbook of Transition Metal Polymerization Catalysts, 2nd ed., John Wiley & Sons Incorporated, Newark 2018.

www.advancedsciencenews.com

- [32] M. Daftaribesheli Ph.D. Thesis, University of Twente, Endschede, The Netherlands 2009.
- [33] P. Mountford, Dalton Trans. 2013, 42, 8977.
- [34] J. R. Severn, in Multimodal Polymers with Supported Catalysts (Eds. A. R. Albunia, F. Prades, D. Jeremic), Springer International Publishing, Cham 2019, p. 1 ff.
- [35] T. F. L. McKenna, M. A. Bashir, in *Multimodal Polymers with Supported Catalysts*, (Eds. A. R. Albunia, F. Prades, D. Jeremic), Springer International Publishing, Cham 2019, p. 81 ff.
- [36] T. F. Mckenna, J. B. P. Soares, Chem. Eng. Sci. 2001, 56, 3931.
- [37] G. G. Hlatky, Chem. Rev. 2000, 100, 1347.
- [38] L. L. Böhm, Macromol. Symp. 2001, 173, 53.
- [39] N. Friederichs, N. Ghalit, W. Xu, in *Tailor-Made Polymers: Via Immobilization of Alpha-Olefin Polymerization Catalysts* (Eds: J. R. Severn, J. C. Chadwick), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany **2008**, p. 211 ff.
- [40] A. Siegmann, I. Raiter, M. Narkis, P. Eyerer, J. Mater. Sci. 1986, 21, 1180.
- [41] A. Salehi, G. Pircheraghi, R. Foudazi, Polymer 2019, 183, 121865.
- [42] L. Hao, M. M. Savalani, Y. Zhang, K. E. Tanner, R. A. Harris, Proc. Inst. Mech. Eng., IMechE Conf. 2006, 220, 125.
- [43] M. Stürzel, S. Mihan, R. Mülhaupt, Chem. Rev. 2016, 116, 1398.
- [44] https://diamond-plastics.de/ 3D Printing Industry. (accessed April 2019).
- [45] G. V. Salmoria, C. H. Ahrens, P. Klauss, R. A. Paggi, R. G. Oliveira, A. Lago, *Mat. Res.* 2007, 10, 211.
- [46] A. Salehi, G. Pircheraghi, J. Appl. Polym. Sci. 2021, 138, 50373.
- [47] J. Bai, B. Zhang, J. Song, G. Bi, P. Wang, J. Wei, *Polym. Test.* 2016, 52, 89.
- [48] J. Zhao, D. Wu, J. Y. Han, Z. Jin, Appl. Mech. Mater. 2014, 633–634, 427.
- [49] W. Sitticharoen, A. Chainawakul, T. Sangkas, Y. Kuntham, Mech. Compos. Mater. 2016, 52, 421.
- [50] G. Alaimo, S. Marconi, L. Costato, F. Auricchio, Composites, Part B 2017, 113, 371.
- [51] H. G. Alt, J. Chem. Soc., Dalton Trans. 1999, 1703.
- [52] G. J. P. Britovsek, V. C. Gibson, D. F. Wass, Angew. Chem., Int. Ed. 1999, 38, 428.
- [53] Catalysis without Precious Metals (Eds: R. M. Bullock), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany 2010.

- [54] Y. Champouret, O. H. Hashmi, M. Visseaux, Coord. Chem. Rev. 2019, 390, 127.
- [55] N. V. Semikolenova, V. A. Zakharov, E. P. Talsi, D. E. Babushkin, A. P. Sobolev, L. G. Echevskaya, M. M. Khysniyarov, J. Mol. Catal. A: Chem. 2002, 182–183, 283.
- [56] J. R. Severn, J. C. Chadwick, R. Duchateau, N. Friederichs, *Chem. Rev.* 2005, 105, 4073.
- [57] M. A. Bashir, V. Monteil, C. Boisson, T. F. L. Mckenna, *React. Chem. Eng.* 2017, 2, 521.
- [58] J. Mazzolini, I. Mokthari, R. Briquel, O. Boyron, F. Delolme, V. Monteil, D. Bertin, D. Gigmes, F. D'agosto, C. Boisson, *Macromolecules* 2010, 43, 7495.
- [59] S. Käselau, S. Scheel, L. Petersson, C.-H. Ho, G. A. Luinstra, *Polym. Int.* 2018, 67, 1359.
- [60] A. Alizadeh, T. F. L. Mckenna, Macromol. React. Eng. 2018, 12, 1700027.
- [61] E. M. Schoeneberger, G. A. Luinstra, Catalysts 2021, 11, 407.
- [62] K. M. Seven, J. M. Cogen, T. Person, J. R. Reffner, J. F. Gilchrist, J. Appl.
- Polym. Sci. 2018, 135, 46325.
 [63] M. Schmid, R. Kleijnen, M. Vetterli, K. Wegener, Appl. Sci. 2017, 7, 462.
- [64] L. Verbelen, S. Dadbakhsh, M. Van Den Eynde, J.-P. Kruth, B. Goderis, P. Van Puyvelde, *Eur. Polym. J.* 2016, 75, 163.
- [65] F. Lupone, E. Padovano, M. Pietroluongo, S. Giudice, O. Ostrovskaya, C. Badini, eXPRESS Polym. Lett. 2021, 15, 177.
- [66] L. J. Tan, W. Zhu, K. Sagar, K. Zhou, Addit. Manuf. 2021, 37, 101610.
- [67] D. Schulze, Powders and Bulk Solids, Springer-Verlag, Berlin 2008.
- [68] T. Laumer, T. Stichel, T. Bock, P. Amend, M. Schmidt, Characterization of Temperature-Dependent Optical Material Properties of Polymer Powders, AIP Publishing LLC, Melville, NY, USA 2015, p. 160001.
- [69] L. J. Tan, W. Zhu, K. Zhou, Adv. Funct. Mater. 2020, 30, 2003062.
- [70] Fraunhofer Direct Digital Manufacturing Conf. DDMC 2020 (Eds: J. S. Evenson, Y. L. Wencke, G. A. Luinstra, C. Emmelmann, B. Müller), Fraunhofer Verlag, Chemnitz 2020.
- [71] M. Yonehara, T.-T. Ikeshoji, T. Nagahama, T. Mizoguchi, M. Tano, T. Yoshimi, H. Kyogoku, Int. J. Adv. Manuf. Technol. 2020, 110, 427.
- [72] Y. Khalil, A. Kowalski, N. Hopkinson, Manuf. Rev. 2016, 3, 15/1.

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Materials and Engineering

4.2 Disentangled UHMWPE@silica powders for potential use in power bed fusion based additive manufacturing

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4.2.1 Synopsis and aim of this research

The effect of the initially lower viscosity and the *melting explosion* make disentangled UHMWPE a perfect candidate for a PBF-polymer ideally leading to the desired mechanical and chemical properties of traditionally shaped UHMWPE parts. The faster entanglement rate should also lead to a much more homogenous entangled melt, which in turn can crystalize more homogenously, resulting in less to no warpage. The previous chapter showed the feasability to synthesize HDPE polymer powders suitable for the PBF process by the catalyst templating polymerization. The next step was to translate these results to the synthesis of disentangled UHMWPE powders. A possible success in processing these new disentangled UHMWPE composites by PBF could lead to products having the outstanding physical properties of UHWMPE combined with the design freedom of powder bed fusion.

The first step consisted of the search for a suitable catalyst capable of generating dUHMWPE. The choice fell on the BROOKHART-GIBSON class of catalysts because of the ease of operation and the ubiquity of the iron center together with the ease of modification of the backbone of the BIP ligand. The next step involved the characterization and identification of the non-templated dUHMWPE. by its characteristic rheologic, mechanical and thermal behavior. Unfortunately, the activation method of the catalyst template used in the previous chapter could not be translated directly to the newly developed catalyst system. A new activation pathway needed to be found. The resulting polymer particles were checked for PBF suitability.

The results of these investigations were published in the following publication.

4.2.2 Manuscript

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Disentangled UHMWPE@silica powders for potential use in power bed fusion based additive manufacturing



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ABSTRACT

Disentangled ultrahigh molecular weight polyethylene dUHMWPE (Mw $\sim 2.10^{6}$ Da) particles in a reactor blend with HDPE are catalytically prepared from ethylene, mediated by a new catalyst from N,N'-(2,6-pyridinediyl diethylidyne) bis[2,6-di-3-propenyl-benzenamine] iron dichloride and triethyl aluminum. These particles could be laser sintered, but not automatically processed in an SLS machine. The same catalyst supported on microsilica particles gives access to composite dUHMWPE@silica particle powder with particle sizes below 200 µm. Testing bars prepared by heat pressing have an Emod of 150 MPa, an elongation at break at 450 % and an ultimate strength of 39 ± 11 MPa. A SEM image indicates a silica induced crystallization into pseudo spherulites of 500 µm size. The dUHMWPE@silica composite particles have an fcc flowability value of 3.4 in a ring shear tester, and a low density of 150 kg.m⁻³. Additivation with nanosilica powder (1 wt%) and carbon black (0.25 wt%) allowed to process the composite in an SLS machine. The printed parts showed severe caking, but also a complete welding of the powder, albeit with voids on account of the low particle density.

1. Introduction

Linear polyethylene with ultrahigh molecular weight ($>10^6$ Da) is notoriously hard to process when it is entangled. The small critical molecular mass of polyethylene gives rise to an unusual high number of entanglements in UHMWPE, which results in exceedingly long relaxation times. The processing is only economical from gels or by compression molding [1]. The latter also leads to the breakdown of chains. The property profile in terms of chemical resistance and mechanics on the other hand, brings UHMWPE in a class of its own when it comes to tensile strength, or friction, impact and fatigue resistance. It also is biocompatible and used in e.g. artificial joints as hip and knee replacements [2,3].

Processing of UHMWPE in 3D printing as an additional procedure bears the promise of getting to the mechanically superior built parts in any form or shape [4–6]. The additive manufacturing (AM) based on laser sintering of powders, PBF/LB/P (powder bed fusion/laser bed/ polymer, aka SLS), probably is the most versatile technology in that regard. The prerequisites for suitable powders are, however, quite extensive and originate from the three designated steps of AM based on PBF, powder recoating, energy input for local melting and powder coalescence followed by solidification [7,8]. Two triad relationships have been introduced to break down the requirements: one for printability and one for printed parts. The printability triad comprises the chemical and morphological properties of the polymer powder that enable processing in an SLS machine. The printed part triad concerns the printing process, melting and solidification together with the properties of the manufactured parts. The final properties of a built part are set within the attainable profile of the material, which would be excellent for UHMWPE and its blends with other polyethylenes [9].

The printability of the powder requires the recoater to reach a dense and uniform layer. Powders with a substantial spherical shape with a smooth surface and an average particle size in range of 10 to 120 μ m with a narrow distribution are favorable in that regard. They should have a reasonable powder flowability (e.g. when characterized in ring shear tester by an fcc of 3 or more). Fusion of the powder by laser light is possible when the powder absorbs the relevant wavelengths. The absorbance is also relevant for diminishing energy scattering, leading to

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a loss of dimensional accuracy of the built part: part of the scattered energy may melt powder outside the scanning range, leading to caking [10].

The powder should have a sinter window in the context of selective laser sintering (SLS), i.e. a workable difference (30 °C) between the onsets of crystallization and melting [7]. The laser sintering should be carried out at a bed temperature within the sinter window. The powder is locally molten by the laser above the crystallization temperature: crystallization best takes only place after solidification once the powder bed is cooled down after completion of the printing job. This procedure should minimize curling and warpage, severe disorders that can result if a uniform crystallization cannot be achieved. In addition, the lasermolten polymer should have the possibility to flow, contacting neighboring particles and underlying layers to form a solid built part, free from voids. The built parts then may reach the level of mechanical strength of the bulk material. The formation of voids is, however, not easy to prevent, i.e. after a first contact of the particle's molten surface, surface tension and capillary forces may be too weak to overcome the viscoelastic resilience of the material against flow [11]. The fusion process is then frozen in the initial state of necking particles, giving porous objects.

The particles favorably have a density close to that of the bulk and have a shape that allows a dense packing to further avoid the presence of voids in the printed part. For UHMWPE, the corresponding powder GUR 2122 from Celanese has been thoroughly characterized in that regard [6]. The particles have an irregular shape, consisting of strands of polymer, and the sinter result is apt for improvement [5]. The sintered parts were porous with a relative density of little over one third with respect to the typical density of PE [12,13].

The option of using disentangled dUHMWPE in AM along SLS is one of generating a low(er) viscous melt and a high strength part as melting dUHMWPE goes along with the formation of entanglements [14,15]. In addition, the crystallization can be modified by the presence of polyethylene waxes, allowing to take influence on curling and warpage [16]. Thermal sintering of UHMWPE thus could lead to superior built parts [17]. The preparation of dUHMWPE is relatively straightforward. Several catalyst systems are reported that do not readily chain terminate and yield UHMWPE in several states of disentanglement [1,18-29]. It is an interplay of catalyst concentration and with that polymer chain concentration, relative polymerization and crystallization rate. The polymerization should effectively be carried out in a way that the action of one catalyst center is not interfered by other catalyst centers, and a newly formed chain can crystallize into individual lamellae without getting entangled with other polymer chains. This can be achieved by dilution in case of homogenous catalysis or by compartmentalization of sites in a supported catalyst [1,24], like in channels of zeolites [30], in droplets of a two-phase system [31], introduction of spacer in form of polyhedral oligomeric silsesquioxane to keep polymer crystals apart [32]. Effectively, also other types of linear polyethylenes directly prepared by polymerization below the melting point may be in a partial disentangled state [32-35]. Most of the entanglements are formed in an early state of polymer formation, when the chain are short and mobile; also classical Ziegler-Natta catalysts can give kind of dUHMWPE when run at relatively low ethylene pressure [36].

UHMWPE can also be kept in a processable state in reactor blends, in particular polyethylene blends prepared by the action of two or more catalysts. A few combinations of homogeneous catalysts with different metals were found useful in that regard [9]. The catalysts were e.g. supported on disintegrating supports, leading to particles in a mm size, favorable for handling in standard slurry or gas phase reactors [33,37]. The resulting products in part are rather porous, which is also unfavorable for application in AM. The choice of support allows to take influence on the morphology of polyethylene particle, i.e. the support may act as a template for the preparation of polyethylene particles [38]. The preparation of smaller and denser particles is feasible starting from integer silica particles. Very recently the preparation of nascent (near) disentangled UHMPE particles with a mean size of 200 μm was reported [39]. The particles were not spherical as no corresponding template was used. It shows, however, that UHMWPE formed in a living polymerization will be in a substantial disentangled state.

We thus set out to prepare dUHMWPE@silica particles in the range below 200 μm by a direct synthesis from ethylene using a silica supported single site iron catalyst. A template-directed particle preparation seemed an attractive method of getting to AM suitable UHMWPE basis. dUHMWPE in bulk cannot be thermoplastically processed without losing the disentangled state, and corresponding particles cannot be prepared from the melt. As a consequence, dUHMWPE is also not available in bulk for milling. The envisioned route of preparation for particles was using a slurry polymerization process with toluene as the medium. Such a procedure would optionally allow incorporating additives for laser light absorption and stabilizers (UV, temperature) in an advanced stage. In this way, an option for preparing UHMWPE built parts by thermoplastic processing or AM with adjustable features would become available.

Bisimine-pyridine iron dichloride complexes (BIP FeCl₂) were chosen as catalyst precursors. The N,N,N ligand frame of bisimine pyridines is easily modified and has been a versatile basis for the preparation of a multitude of iron(II) dichloride polymerization and other catalysts [40,41]. The choice of ligand allows to tune the complex in combination with an activator from an ethylene oligomerization catalyst to a system generating high molecular weight polyethylene. The catalyst system can readily be supported on silica and other carriers keeping its high activity, and is still subject of recent developments [42–48]. The family of iron catalysts would allow to choose a combination for the preparation of a blend of polyethylenes, as they have various modes of polyethylene formation. It thus seems useful to extent this technology, as it has been shown that PE prepared on a support can be tuned in their flow properties by using a combination of catalysts [33,49–52].

2. Experimental

2.1. Materials

All manipulation of air- and/or moisture-sensitive compounds was carried out under a dry nitrogen atmosphere using standard Schlenktechniques. Micro-sized silica in form of Perkasil 300 KS was generously supplied by W. R. Grace and Company. UHMWPE was a gift from Celanese Corporation. Aniline was purchased from SIAL and used without further purification. Allyl bromide and sodium carbonate were purchased from Merck. Magnesium sulfate was purchased from Grüssing. Xylene was purchased from Kraft. Absolute diethyl ether, BF₃ etherate solution, *para*-toluenesulfonic acid, 2,6-diacetylpyridine, iron dichloride, methanol, 1-butanol and ethanol were purchased from Sigma-Aldrich. All these compounds were used without further purification. CDCl₃ was purchased from Deutero GmbH.

2.2. Synthesis of 2,6–Bis[1–(2,6-dipropen-3-yl phenylimino) ethyl] pyridine

2,6-Diacetylpyridine (0.17 g, 1.0 mmol), 2,6–diallyl aniline (0.99 g, 5.7 mmol, 5.7 equiv.), *p*-toluene sulfonic acid (56 mg, 280 μ mol, 28 mol %) and ~ 1 g molecular sieve type 4 Å were suspended in 6 mL absolute toluene under an nitrogen atmosphere. The reaction mixture was refluxed for 20 h. After cooling to room temperature, the solution was reduced *in vacuo* to 3 mL and 100 mL of methanol were added. The mixture was held at –18 °C for 48 h. The precipitated crystals were collected on a filter frit and washed with methanol. Yield: 0.17 g, 360 µmol, 36 %.

¹H NMR (600 MHz, CDCl₃): δ [ppm] = 8.51 (d, J = 7.8 Hz, 1H, H-2), 7.94 (t, J = 7.8 Hz, 1H, H-3), 7.15 (d, J = 7.6 Hz, 4H, H-8), 7.06 (d, J = 7.6 Hz, 2H, H-9), 5.94 – 5.86 (m, 4H, H-11), 5.03– 4.97 (m, 8H, H-12), 3.18 (ddd, J = 22.9, 15.5, 6.7 Hz, 8H, H-10), 2.25 (s, 6H, H-5).

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Scheme 1. Synthesis of the ligand.

¹³C NMR (151 MHz, CDCl₃): δ [ppm] = 136.9 (C-3),136.5 (C-11), 135.9 (C-9), 128.5 (C-4), 128.0 (C-6), 127.6 (C-8), 127.6 (C-2), 123.6 (C-1), 122.7 (C-7), 115.9 (C-12), 36.1 (C-10), 17.4 (C-5) (assignments are in Scheme 1).

2.3. Synthesis of 2,6–Bis[1–(2,6-dipropenylphenylimino)ethyl]pyridine iron(II) dichloride

Iron(II) dichloride (27.8 mg, 219 µmol) was dissolved in 4 mL absolute *n*-butanol at room temperature under an nitrogen blanket. 2,6-bis [1-(2,6-diallylphenylimino)ethyl]pyridine (53.1 mg, 112 µmol, 0.5 equiv.) was added. The yellow solution turned instantaneous blue and a blue powder precipitated. 3 mL of absolute diethyl ether was added to the reaction mixture and the blue powder was collected on a filter frit. The residue was dried *in vacuo* to give a dark blue solid. Yield: 47.7 mg, 71 %, 79 µmol. ¹H NMR (400 MHz, CDCl₃, paramagnetic): δ [ppm] = 78.65, 48.63, 15.27, 10.46, 1.82, 0.90, -1.32, -27.36. ESI-MS: *m*/*z* = 564.19 ([M–Cl]), 474.30 ([M - FeCl₂]). MALDI-MS: *m*/*z* = 599.144 ([M]), 564.176 ([M - Cl)

2.4. Microsized separated silica particles

Perkasil 300 KS was dispersed in water by ultrasound impact. Typically, 22.5 g of Perkasil were added to 277.5 mL of deionized water. The dispersion was subjected 3 times to 10 min ultrasonic impact with a Sonopuls 2070 of the company Bandelin equipped with a V70T Sonotrode head at 80 % amplitude. Subsequent spray drying was performed on a Minispray Dryer 290 with an inert loop B-295 of the company Büchi. It was executed with the aspirator at 80%, the pump at 40 % and the pressurized air at 30 % of maximum capacity. The inlet temperature was 180 °C and the outlet temperature 77 °C.

2.5. Catalyst support

Spray dried silica (1 g) was dried in a dynamic vacuum at 150 °C for 2.5 h. Subsequently, in an evacuated Schlenk vial the desired amount of precatalyst 1 suspended in dry toluene and dry dichloromethane were added (typically 2 mL of 2.4 mM 1 in toluene, 4 mL of dichloromethane). The blue solution was transferred to the silica and mixed using a laboratory mixer. The resulting slurry evaporated to dryness until a light blue, free flowing powder was received.

2.6. Ethylene polymerization

Polymerizations were performed within a Büchi miniplant reactor with supply of solvent, gases/vacuum and olefins. A 1 L glass reactor was used in this study, connected to the ethylene supply by a massflow controller. Toluene for polymerizations was supplied from Merck and purified by distillation and passing through columns filled with molecular sieve (4 Å) and BASF catalyst R3-11/G. Ethylene was purchased from Westfalen AG and was purified by passing through columns filled with molecular sieve (4 Å) and BASF catalyst R3-11/G. Triethyl aluminum (TEA) was purchased as a 25 wt% solution in toluene from Sigma-Aldrich and used as received. MAO was purchased from Crompton as a 10 % solution in toluene and used as received.

Polymerization was performed by filling the reactor with 600 mL of toluene, adding cocatalyst by syringe (MAO to a level of 2.8 mmol/L⁻¹ or TEA to 3.0 mmol.L⁻¹). The solvent was saturated with ethylene gas (addition via the gas phase) to a constant pressure of 3 bars at reaction temperature. Subsequently catalyst (support/non-supported) was added as a suspension in 6 mL of toluene. After reaching the preset reaction time, the excess ethylene was discharged and the reaction was quenched by the addition of small aliquots (5 – 20 mL) of ethanol. The resulting slurry was mixed with ~ 1.5 L of ethanol and the residue collected and filtered. The white powder was dried *in vacuo* at 40 °C. The silica content was calculated from the isolated yield and the amount of silica used, assuming a complete incorporation.

2.7. Powder addition

The synthesized polyethylene particles were mixed with carbon black Ketjenblack EC 300 J (Weber und Schaer, Hamburg, Hamburg, Germany) and additionally with silicon dioxide nanoparticles (Ionic Liquids Technologies GmbH, Heilbronn, Baden-Württemberg, Germany). Mixing was performed separately for each additive, using a Speedmixer DAC 400 (Hauschild & Co KG, Hamm, North Rhine-Westphalia, Germany), switching between a cooling step, where the mixing container is cooled with ice water, and a mixing step with 2500 rpm for one minute, for a total of five cycles for each additive.

2.8. Methods

NMR-data was obtained using a Bruker AVANCEIII HD 400 MHz spectrometer. 1–5 mg of each sample were dissolved in 0.7 mL of water and acid free CDCl₃ and measured at room temperature. SEM images were obtained on a LEO 1525 Gemini scanning electron microscope after coating with carbon. Samples were coated with carbon using a Leica ACE 600 (both: Wetzlar, Hesse, Germany). Micrographs were recorded with an acceleration voltage of 5 kV.

High temperature size exclusion chromatography for the determination of the molecular weight distributions were executed using a PL-GPC-220 of the company Agilent. The instrument was equipped with a refractive index detector and 1,2,4-trichloro benzene was used as solvent. Measurements were executed at 135 °C and evaluated using a polystyrene calibration. The results of SEC experiments were transformed to (close to) absolute numbers by an universal calibration procedure using the Kuhn-Mark-Houwink-Sakurada equation [53].

Melting and crystallization of the polymer composites was investigated using a DSC1 of the company Mettler Toledo (Columbus, Ohio, United States). Standard non-isothermal crystallization experiments were executed for all samples by a heating from 25 °C to 180 °C at a heating rate of 10 K·min⁻¹. The sample was held at 180 °C for 5 min and then cooled to 25 °C with a cooling rate of 10 K min⁻¹. After holding the sample at this temperature, the sample was subjected to a second heating and cooling cycle with the same parameters as above. All experiments were executed in an inert nitrogen atmosphere.



Scheme 2. Preparation and structure of the precatalyst 1.

Annealing experiments were performed according to an adapted procedure [54]. Samples were heated close to the melting range of the material (135.6 °C/136 °C) and left to anneal at this temperature for a set amount of time. After this annealing step, the sample was cooled down to 50 °C with 10 K.min⁻¹ and held at this temperature for 5 min. The protocol then consists of a heating step to 160 °C with a heating rate of 10 K.min⁻¹. After holding this temperature for 5 min the cooling and heating step were repeated once again. All experiments were executed in an inert nitrogen atmosphere.

Heat sintering was performed in mold of 100*100*1 mm³. The powder was heated to 200 °C while applying a pressure of 200 bars. After 10 min of pressing, the mold was allowed to slowly cool to room temperature. Tensile test specimens derived from DIN EN ISO 527-5A were prepared from a heat pressed plate by die cutting. Tensile testing was performed subsequently on a Zwicki-Line Z1.0 of the company ZwickRoell (Ulm, Baden-Württemberg, Germany) with 1 kN force transducer and a crosshead speed of 50 mm.min⁻¹ and at 23 °C. Samples were kept at that temperature and under the exclusion of moisture prior to measurement.

Particle size and distribution of the polymer powders and composites were measured on a HELOS KR laser diffraction sensor equipped with a RODOS/GRADIS dry dispersion setup of the company Sympatec (Clausthal-Zellerfeld, Lower Saxony, Germany). Particle roundness was determined by a dynamic image analysis according to ISO 13322–2 with a Camsizer XT of the company Retsch. (Haan, North-Rhine-Westfalia, Germany). Powder flowabillity measurements were executed on a ring-shear-tester RST-XS.s of the company Dietmar Schulze (Wolfenbüttel, Lower Saxony, Germany). A sample of 20 g was placed inside the ring shear tester and subjected to a pressure of 500 Pa. Measurements were subsequently performed at 75 Pa intervals lower until to 200 Pa.

Rheological measurements were performed on polymer samples thermally stabilized with Irganox 1010 [54]. Thus, Irganox 1010 was dissolved in acetone and polymer particles were added to give a suspension. The solvent was subsequently removed *in vacuo* until a dry polymer powder resulted with 0.5 wt% Irganox 1010. Discs of 25 mm in diameter were prepared by compressing 1 g of polymer powder in a hot press at 200 bars of pressure and 125 °C. The received discs were subsequently heated in an AR 2000 (Texas Instruments) rheometer to 160 °C at zero force. The time sweep experiment was executed under constant axial force of 4 N, an angular frequency of 10 rad/s and a strain of 0.2 %.

Table 1 Ethylene polymerization by precatalyst 1 in combination with TEA.

2.9. Powder bed Fusion.

A reduced building chamber, housed inside a commercial PBF machine (EOS P390), was designed and built to allow the testing of smaller amounts of material [55]. Several issues had to be resolved, such as correlating the set point temperature and the actual temperature on the powder surface, adjusting the gap distance between parts so no powder leakages occur and insulating/heating the build chamber. Laser parameters used were a laser power of 36 W, a scanning speed of 1500 mm. s⁻¹, and a hatch distance of 0.15 mm. The temperatures set were 122.5 °C in the process chamber and 120 °C in the removal chamber.

3. Results and discussion

3.1. Catalyst synthesis and product characterization

A serendipitous finding led to the discovery of a BIP FeCl₂ catalyst for the synthesis of dUHMWPE. The complex **1** with the ligand N,N'-(2,6pyridinediyldiethylidyne) bis[2,6-di-2-propenyl] benzenamine was prepared in the context of enhancing the solubility of the complexes. The ligand was originally chosen as a precursor for further derivatives. The propenyl benzenamine is readily available from aniline and allyl bromide after N-addition and an aza-Claisen rearrangement [56]. A standard condensation with 2,6-diacetyl pyridine gives the final ligand, and complexation to iron dichloride gives the usual blue precatalyst **1** (Scheme 2). The complex is reasonably stable in dry air, and can be handled just like standard BIP FeCl₂ catalysts without special precautions.

Polymerization of ethylene by 1 can be achieved in toluene solvent after activation with triethyl aluminum (TEA) below room temperature. Surprisingly, the complex cannot be activated with methyl aluminoxane (MAO) for ethylene polymerization at those temperatures in a reasonable time frame. No polymerization activity was found over a period of 30 min at 0 °C at a concentration of 2.4 μ mol.L⁻¹ and concentrations of MAO between 0.28 mmol.L⁻¹ and 2.8 mmol.L⁻¹ (Table 1). This low temperature was chosen for the lower swelling of the polymeric product. Typical BIP FeCl₂ complexes like those based on ligands prepared from ortho alkyl substituted anilines become active ethylene polymerization catalysts in combination with MAO at such temperatures [57]. The expected color change from blue to orange did also not occur. Most of the BIP FeCl₂ complexes show this color change directly after contact with MAO. Instead, a color change to brown/green is observed, only at higher temperatures (40 °C) the complex turns red–orange (in a period of

entry		1 - 1	time	yield	activity	M _w (SEC)	PDI
	cocatalyst	mmol.L*	[min]	[g]	[t.(mol bar h)^]	[10° g.mol ^]	
1	MAO	0.28	30	_			
2	MAO	2.8	30	-			
3	TEA	3	30	7.68	3.6	2.87	47
4	TEA	3	7.5	1.59	2.9	2.14	126

Reaction conditions: 0 °C, 2.4 µmol.L⁻¹ of 1, 600 mL of toluene, 3 bar of ethylene, 500 RPM.



Fig. 1. Molecular weight distribution of the action of precatalyst 1 with TEA.



Fig. 2. DSC Measurement of maiden dUHMWPE/HDPE blend (10 °C.min⁻¹).

several minutes). BIP iron complexes with a single *ortho*-propenyl entity were prepared in the past, they are readily activated by MAO [58]. Apparently, a barrier exist for obtaining the MAO activated complex 1 when four propenyl moieties are in the ligand sphere.

TEA acts as expected as both an activator and chain transfer agent. Polymerization of ethylene at 3 bars of pressure in semi-batch gave catalyst activities in the range of $2-4 \ 10^6$ g.(mol Fe·bar·h)⁻¹ (Table 1). Although no specific screening for polymerization conditions was

carried out, these conditions are generally useful for a controlled synthesis of polyethylenes with such BIP FeCl₂ complexes [57–59]. The polymer was isolated after the excess ethylene was discharged, and the reaction was quenched by the addition of small aliquots (5 – 20 mL) of ethanol. The products were dried in a temperature range below 40 °C to keep the product in a pristine state.

The bimodal distribution of the product shows polyethylene of low mass (~2 10^4 Da), resulting from chain transfer to aluminum with consecutive precipitation and UHMWPE (M_w of ~ $2 \cdot 10^6$ Da) [57]. Longer reaction times lead to more UHMWPE (Fig. 1). The formation of such high molecular weight polyethylene is not observed with BIP catalysts having only one propenyl entity per aniline in the ligand, not even at 10 bars of ethylene pressure. It is, however, found that the presence of propenyl entities enhances the molecular weight of the formed polyethylene, which is even more extensive in the catalysis with complex 1 [58].

Thus, the typical reactor blends of HDPE/UHMWPE were obtained with only one catalyst in form of 1 [9,16,60–62]. The ratio of HDPE to UMWPE would be adjustable by the reaction time or TEA concentration, however, this was not pursued here [63]. Whether the catalyst is incorporated into the polymer by an allylic insertion was also not the focus of this project, and was not addressed [58,64–66].

The DCSs show one melting isotherm, like is typical for in situ blends with single supports [49,67–69]. The thermal properties of the polymer are typical for not (fully) entangled UHMWPE [61]. The pristine material had a first (standard) melting point of 142.1 °C and a high degree of crystallinity of 73 % [27,70]. These properties were not restored after cooling the once molten sample from the molten state (Fig. 2). The second heating showed a material with melt temperature of 138.5 °C and the crystallinity decreased to 53 %. This behavior is in line with the loss of the disentangled state with its characteristic high crystalline content [24].

DSC-annealing experiments were carried out to investigate the disentangled state. These thermal experiments comprise an annealing step close to the melting point for a set time before a regular DSC-protocol with a heat rate of 10 °C.min⁻¹ is executed (Table S1). The annealing temperature was a compromise of the second melting points of the samples after annealing at 137 °C (Table S1). The evolution of a secondary lower melting point is found with increasing annealing time. The lower peak corresponds to the melt crystalized material (~136 °C) while the higher melting peak (~140 °C) correspond to the nascent nonmolten polymer crystals. Again, this is typical for melting of disentangled polyethylene, wherein lamellae detachment from nascent polymer crystals occurs. These detached chains can entangle and recrystallize upon cooling at a lower temperature [15,54]. Commercial entangled UHMWPE (GUR 4150–3: Mw: 8.1 10⁶ g/mol and GUR 4012

Fig. 3. A: Normalized peak area of the melting peaks from DSC annealing experiments with annealing time (left; A1: area at 136 °C, A2: at 141 °C); B: Development of the elastic modulus over time (right; 160 °C, 10 rad.s⁻¹, 0.2 % strain [54]).

5

Fig. 4. SEM image of a nascent UHMWPE particle.

Mw: 1.7 10⁶ g/mol) does not show this behavior to the same extent, and the time scale of detachment is longer as the higher amount of entanglements in the polymer crystals hinders the smooth and faster lamellae reorganization even in the sample of GUR 4012 with a similar molecular weight (Fig. 3A). A further indicator of the disentangled state of the polymer is that the characteristic elastic modulus G' increases in time upon first melting of a nascent polymer sample. The elastic modulus of the pristine dUHMWPE sample upon first melting is lower in the maiden state because of the molecular weight and fewer entanglements compared to commercial UHMWPE grades (Fig. 3B).

In addition, samples of blends pressed below the melting temperature (125 °C) into tapes [71] were well stretchable using the "hot shoe technique", while polymer samples pressed above the melting point (180 °C) appear quite brittle (Figure S2) [72]. The disentangled polymer chains in the cold-pressed sample slowly rearranged and aligned themselves in long fibers during the stretching procedure (Figure S3). European Polymer Journal 163 (2022) 110936

The polymer chain segments in the hot-pressed sample could not slip past each other within the time frame of elongation, resulting an earlier mechanical failure.

3.2. Laser sintering of the dUHMWPE powder

The isolated powdery polymer showed no particular useful flowability, probably on account of the wide distribution of particle sizes and the irregular shapes and agglomerates. In addition, the surface of identified particle-like entities was not particular smooth (Fig. 4). The potential of the dUHMWPE blend for obtaining SLS built parts was nevertheless screened in a rudimentary experiment to obtain a proof of concept. One batch of isolated blend powder was therefore sieved to receive a sample that could be manipulated/flattened by the recoater of an EOSINT P 390 (EOS GmbH) SLS machine. Laser sintering at a temperature of the building chamber of 122 °C allowed fusion of the particles. A second layer could be applied and subsequent sintering gave essentially a 2D object with a geometry according to ISO 527–2 Type 5B (Figure S2).

The blend particles had fused together resulting in a shrinkage on account of a distinct melt flow of the low-density precursor (Fig. 5). The powder obviously had been completely molten in the focus of the laser beam (Fig. 5AB), and a substantial coalescence had taken place. This was taken as a promising observation for the approach of using disentangled particulate UHMWPE for the preparation of 3D objects by PBF/LB/P. Voids were regularly present, showing that the flow leading to densification and the concomitant increase of viscosity was too fast for the air to leave the sample. The low inherent density of the particles next to the anticipated loose packing of the spiky outside should also be improved. Non-molten particles adhered to the laser molten welded part, and some caking was observed (Fig. 5CD).

Fig. 5. SEM images of laser sintered dUMWPE/HDPE blends. A: Side view of cryo-fractured sample with a molten layer on top (100 x). B: Top view of laser sintered tensile specimen (100 x). C: Interface between molten layer and agglomerated particles (2 K x). D: Agglomerates beneath molten layer (1.5 K x).

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Fig. 6. SEM micrographs of dUHMWPE@silica synthesized with 1 supported on spray dried silica microparticles. Reaction conditions: 8 µmol.L⁻¹ 1 on 1 g of spray dried silica microparticles, 9 mmol.L⁻¹ TEA, 20 °C, 3 bar of ethylene, 200 RPM, 600 mL of toluene, 60 min.

Fig. 7. Particle size distributions for dUHMWPE@silica particles. Reaction conditions: 8 μ mol.L⁻¹ 1 on 1 g of silica microparticles, 9 mmol.L⁻¹ of TEA, 20 °C, 3 bar of ethylene, 200 RPM, 600 mL of toluene, 60 min of reaction time.

 Table 2

 Tensile properties of press sintered GUR UHMWPE and dUHMWPE samples.

	Yield stress [MPa]	Young modulus [MPa]	Ultimate tensile stress [MPa]	Elongation at break [%]
GUR 4150-3	16.8 ± 0.7	148 ± 38	44 ± 9	$\textbf{492} \pm \textbf{65}$
dUHMWPE@silica	21.2 ± 0.5	156 ± 32	39 ± 11	450 ± 19

3.3. Silica template synthesis of HDPE/dUHMWPE blends

Next, a template synthesis of the polyethylene blend was targeted using a commercial available source of silica microparticles (in the following, dUHMWPE should be understood as the HDPE/dUHMWPE blend). It was found useful for obtaining more or less agglomerate free, spherical particle to redisperse the silica in water and re-isolate the particles by spray drying. The catalyst was applied molecularly to this support from a dichloro methane solution. A light blue, free-flowing powder was obtained after evaporating the solvent. The collected powder was dispersed in toluene and injected into a reactor charged with toluene and TEA. Prior to the addition of the catalyst, the toluene was saturated with ethylene at 3 bars of pressure. The reaction again was carried in semi-batch mode, now at 20 °C, continuously feeding ethylene to keep the pressure constant. The higher temperature was necessary for obtaining an acceptable activity.

A polyethylene shell was formed around the silica making up 96 % of the solid mass after 60 min. The resulting particles had an in essence spherical but somewhat irregular shape. Mostly individual particles are present, adhered into smaller, loose agglomerates (Fig. 6). The particles appear more compact than those prepared without a template, but still are porous and have a course surface. Individual lamellae are indicated in the SEM images. DLS analysis showed a more or less template copied particle size distribution with a median size of 85.5 \pm 0.8 μ m (Fig. 7). The shape of the distribution at the larger size range has a diffuse cut-off at about 200 μ m, reminiscent of the presence of some agglomerates that do not breakup. The templating effect (replication) by the simple procedure thus was reasonably successful with respect to size and shape, but is also apt for improvement with respect to density and surface smoothness.

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Fig. 8. SEM micrographs of a cryo-fractured press sintered dUHMWPE@silica sample with 3.9 wt% of silica.

3.4. Material properties of heat pressed dUHMWPE@silica

The tensile properties of thermal press sintered testing bars of the dUHMWPE@silica are in the range of similarly treated commercial UHMWPE (Figure S4; Table 2). Tensile test bars derived from DIN EN ISO 527-5A were manufactured by die cutting specimens from hot pressed plates. The stress strain behavior is the usual for a high molecular weight polyethylene with a yield point and strain hardening. Tensile testing of similarly processed commercial UHMWPE powder material (GUR 4150-3) with a very high molecular weight (My of $9*10^{6}$ Da) as benchmark showed a yield strength of 16.8 \pm 0.7 MPa. It remains somewhat short of reported values (20 - 25 MPa) [73,74]. The formation of new entanglements may have needed more time [15]. The silica templated dUHMWPE based testing bar showed a higher yield point of up to 21.2 ± 0.5 MPa. The Young modulus, ultimate stress and elongation at break are somewhat lower than reported values, but statistically not different between the considered hot pressed materials (Table 2). The presence of 3.9 % of microsilica in the dUHMWPE blend and the lower molecular weight with a bimodal distribution may account for the differences in mean values.

Cryobreaking of the dUHMWPE@silica testing bar gives an even, flat breaking surface with no fiber pullouts. In contrast, the corresponding GUR UHMWPE sample shows a rough and uneven surface reminiscent of the originating particle conglomerate [75]. This shows that also in case of the template synthesis with 1, disentangled (mobile) polyethylene is formed.

The structure of the press-sintered sample shows an unusual pattern with large crystallized spherical, spherulite like structures with clear boundaries (Fig. 8). The size of the structures is in the range of $200 - 400 \mu$ m. They possibly have a silica center as was concluded from the size of the recognizable higher density in the middle that is in the range of the parent silica particles. The spheres are embedded in apparently a more continuous matrix. The size of the structure reaches well-beyond that of the original particles; a complete reorganization of the polyethylene from the melt has taken place. These structures are not present in the heat pressed samples of commercial UHMWPE, their morphology shows a more granular structure at the size of originating particles (Figure S5) [75]. These new dUHMWPE particles thus may find use in procedures with thermal shaping to UHMWPE parts.

The onset of melting and crystallization of the dUHMWPE@silica is 129.8 resp. 119.3 °C, a laser sinter window results of about 10 °C. This is an even smaller value than for GUR 4150–3 of about 15 °C (**Table S3**), possibly originating from the nucleating action of the silica microparticulate template in combination with the HDPE part in dUHMW-PE@silica [15]. A very accurate temperature control in SLS thus has become necessary [76].

The flowability of the dUHMWPE@silica has an fcc value of 3.44 in a

Table 3

Flow function, bulk density, and sphericity of dUHMWPE@silica.

source	ffc (500 Pa)	Bulk density [kg.m ^{—3}]	Sphericity
as synthesized	3.44	130	0.55
after high energy mixing	2.31	115	0.54
additivition with 1 wt% silica & 0.25 wt % CB	2.59	72	0.58

ring shear tester. This number seemed too low for handling by a recoater in an SLS machine. Former experience with GUR 4150–3 had shown that processing in a speed mixer could improve the flowability of the powder. High energy impact on dUHMWPE@silica in a dual asymmetric centrifuge, however, led to a substantial decrease of the fcc value to 2.31. The sphericity was in the ~ 0.55 region and did not change much with high energy mixing, but the bulk density decreased by more than 1 unit (Table 3). The packing of the particles obviously became worse, possibly by an increase of edges, interlocking them and/or by the formation of fines. dUHMWPE crystallites may have been lost from the particles or from the agglomerates.

The high energy treated dUHMWPE@silica particles were subsequently additivated with 1 wt% of nanosilica powder and 0.25 wt% of carbon black CB before screening in SLS. Nanosilica was used for its positive action on the flowability, which indeed restored some but not all of the flowability [5]. The CB was used for the low-density powder for absorbing reflected laser light. The addivation led even to a less dense powder with a density of 72 kg.m⁻³. An optimization clearly is a project on its own, and will follow in the course of our current efforts after the parent UHMWPE@silica powder is further studied.

Despite the not too favorable properties of the dUHMWPE@silica

Fig. 9. Set of tensile test specimens of the type 1bb of dUHMWPE@silica with the addition of 1 wt% of nano silica and 0.25 wt% of CB built by PBF with the best practice parameters.

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Fig. 10. SEM micrographs of the cryo-fractured tensile test specimens and its top surface of dUHMWPE with 1 wt% of nano silica and 0.25 wt% of CB built by PBF.

powders, orientating SLS experiments were performed. This was done also with the objective to assess the potential of the route for being useful in the preparation of UMWPE parts with properties close to those of bulk material. It was already clear, that several stages in the approach would need further attention. Initially found best practice parameters of a small study on printing HDPE powders were used in the operation of the printer. Latter study was performed in a miniaturized set up, allowing to sinter also research quantities of material [55].

Disappointingly, the built parts in form of testing bars showed a large amount of caking and could not be separated (Fig. 9). Scattering of laser light could not effectively be prevented by the added CB, leading to hardly recognizable printed testing bars. The low-density powder was taking up enough thermal energy to fully melt, inclusive its immediate surrounding. The surface of the built part, however, was very course and breaking the ensemble was easy. SEM micrographs revealed that the structure of the intended testing bars consisted of few consolidated droplets of polymer melt but a solid part had not formed (Fig. 10). The very low bulk density of the powder may be the cause for this. The break surface of such a droplet was clean and even with few pores, indicating again a good welding. These results display the general possibility of manufacturing parts of dUHMWPE with a PBF process. However, the bulk density of the powders needs to be increased. Current research is directed toward this.

4. Conclusions

A new BIP iron(II) catalyst was discovered that is activated by TEA to give a blend of HDPE and substantially disentangled UHMWPE. Laser sintering of the material is possible and the result indicated that a good welding is possible, i.e. a low viscous melt can be generated that fuses to a solid 2D object with some voids. The complex can be supported on micro-sized silica to give a template for HDPE/dUHMWPE@silica particles in a range below 200 μ m. Thermal sintering of the powder gives a material with typical UHMWPE properties. The morphology shows that the powder has been fully molten and a crystallization initiated from the silica particles gives an unusual internal structure. The sphericity and flow properties of the dUHMWPE@silica are promising, however, the particles need optimization with respect to density and packing for making them more suitable for 3D printing along PBF/LB/P.

CRediT authorship contribution statement

Yannick L. Wencke: Investigation, Formal analysis, Writing – original draft, Visualization. Gerrit A. Luinstra: Funding acquisition, Conceptualization, Writing – review & editing, Supervision. Rob Duchateau: Writing – review & editing. Friedrich Proes: Investigation, Writing – review & editing. Philipp Imgrund: Project administration. Jonathan S. Evenson: Investigation. Claus Emmelmann: Funding acquisition, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary material

Supplementary data to this article can be found online at https://doi. org/10.1016/j.eurpolymj.2021.110936.

References

- K. Patel, S.H. Chikkali, S. Sivaram, Ultrahigh molecular weight polyethylene: Catalysis, structure, properties, processing and applications, Prog. Polym. Sci. 109 (2020) 101290, https://doi.org/10.1016/j.progpolymsci.2020.101290.
- [2] S.M. Kurtz (Ed.), UHMWPE biomaterials handbook: Ultra high molecular weight polyethylene in total joint replacement and medical devices, William Andrew an imprint of Elsevier, Amsterdam, Boston, (2016).
- [3] S. Changhui, H. Aibing, Y. Yongqiang, W. Di, Y.u. Jia-kuo, Customized UHMWPE tibial insert directly fabricated by selective laser sintering, Int. J. Adv. Manuf. Technol. 85 (5-8) (2016) 1217–1226, https://doi.org/10.1007/s00170-015-8046-6
- [4] R.D. Goodridge, R.J.M. Hague, C.J. Tuck, An empirical study into laser sintering of ultra-high molecular weight polyethylene (UHMWPE), J. Mater. Process. Technol. 210 (1) (2010) 72–80, https://doi.org/10.1016/j.jmatprotec.2009.08.016.
- [5] X. Zhu, Q.i. Yang, Sintering the feasibility improvement and mechanical property of UHMWPE via selective laser sintering, Plast. Rubber Compos. 49 (3) (2020) 116–126, https://doi.org/10.1080/14658011.2020.1718321.
- [6] Y. Khalil, N. Hopkinson, A. Kowalski, J.P.A. Fairclough, Characterisation of UHMWPE polymer powder for laser sintering, Materials 12 (2019) 3496, https:// doi.org/10.3390/ma12213496.
- [7] C.A. Chatham, T.E. Long, C.B. Williams, A review of the process physics and material screening methods for polymer powder bed fusion additive manufacturing, Prog. Polym. Sci. 93 (2019) 68–95, https://doi.org/10.1016/j. progpolymsci.2019.03.003.
- [8] R. Brighenti, M.P. Cosma, L. Marsavina, A. Spagnoli, M. Terzano, Laser-based additively manufactured polymers: a review on processes and mechanical models, J. Mater. Sci. 56 (2) (2021) 961–998, https://doi.org/10.1007/s10853-020-05254-6.
- [9] M. Stürzel, S. Mihan, R. Mülhaupt, From Multisite Polymerization Catalysis to Sustainable Materials and All-Polyolefin Composites, Chem. Rev. 116 (3) (2016) 1398–1433, https://doi.org/10.1021/acs.chemrev.5b00310.
- [10] H. Scholten, W. Christoph, Use of a polyamide 12 for selective laser sintering. CAPLUS AN 1999:279704(Patent), Eur. Pat. Appl. Copyright © 2021 American Chemical Society (ACS). All Rights Reserved 7 pp.
- [11] C.T. Bellehumeur, M.K. Bisaria, J. Vlachopoulos, An experimental study and model assessment of polymer sintering, Polym. Eng. Sci. 36 (17) (1996) 2198–2207, https://doi.org/10.1002/pen.10617.
- [12] Y. Khalil, A. Kowalski, N. Hopkinson, Influence of laser power on tensile properties and material characteristics of laser-sintered UHMWPE, Manuf. Rev. 3 (2016) 15/ 1-15/9, https://doi.org/10.1051/mfreview/2016015.
- [13] J.T. Rimell, P.M. Marquis, Selective laser sintering of ultra high molecular weight polyethylene for clinical applications, J. Biomed. Mater. Res. 53 (2000) 414–420, https://doi.org/10.1002/1097-4636(2000)53:4<414:AID-JBM16>3.0.CO;2-M.
- [14] A. Galeski, M. Psarski, Morphology and kinetics of crystallization of polyethylene from chain disentangled melt, Macromol. Symp. 104 (1) (1996) 183–190, https:// doi.org/10.1002/masy.19961040118.
- [15] T. Deplancke, O. Lame, F. Rousset, I. Aguili, R. Seguela, G. Vigier, Diffusion versus Cocrystallization of Very Long Polymer Chains at Interfaces: Experimental Study of Sintering of UHMWPE Nascent Powder, Macromolecules (Washington, DC, U. S.) 47 (2014) 197–207. https://doi.org/10.1021/ma402012f.
- [16] D. Hofmann, A. Kurek, R. Thomann, J. Schwabe, S. Mark, M. Enders, T. Hees, R. Mülhaupt, Tailored Nanostructured HDPE Wax/UHIMWPE Reactor Blends as Additives for Melt-Processable All-Polyethylene Composites and in Situ UHMWPE Fiber Reinforcement, Macromolecules (Washington, DC, U. S.) 50 (2017) 8129–8139. https://doi.org/10.1021/acs.macromol.7b01891.
- [17] M. Rezaei, N.G. Ebrahimi, M. Kontopoulou, Thermal properties, rheology and sintering of ultra high molecular weight polyethylene and its composites with polyethylene terephthalate, Polym. Eng. Sci. 45 (5) (2005) 678–686, https://doi. org/10.1002/pen.20319.
- [18] D. Romano, S. Ronca, S. Rastogi, A hemi-metallocene chromium catalyst with trimethylaluminum-free methylaluminoxane for the synthesis of disentangled ultra-high molecular weight polyethylene, Macromol. Rapid Commun. 36 (3) (2015) 327–331, https://doi.org/10.1002/marc.201400514.
 [19] I.V. Oleynik, I.K. Shundrina, I.I. Oleyinik, Highly active titanium(IV) dichloride FI
- [19] I.V. Oleynik, I.K. Shundrina, I.I. Oleyinik, Highly active titanium(IV) dichloride FI catalysts bearing a diallylamino group for the synthesis of disentangled UHMWPE, Polym. Adv. Technol. 31 (2020) 1921–1934, https://doi.org/10.1002/pat.4917.
- [20] A. Heidari, H. Zarghami, S. Talebi, M. Rezaei, A disentangled state using TiCl4/ MgCl2 catalyst: a case study of polyethylene, Iran, Polym. J. 27 (9) (2018) 701-708, https://doi.org/10.1007/s13726-018-0648-z.
- [21] A. Pandey, Y. Champouret, S. Rastogi, Heterogeneity in the Distribution of Entanglement Density during Polymerization in Disentangled Ultrahigh Molecular Weight Polyethylene, Macromolecules (Washington, DC, U. S.) 44 (2011) 4952–4960. https://doi.org/10.1021/ma2003689.

European Polymer Journal 163 (2022) 110936

- [22] G. Forte, S. Ronca, Synthesis of Disentangled Ultra-High Molecular Weight Polyethylene: Influence of Reaction Medium on Material Properties, Int. J. Polym. Sci. 2017 (2017) 1–8, https://doi.org/10.1155/2017/7431419.
- [23] A. Petrov, V.Y. Rudyak, P. Kos, A. Chertovich, Polymerization of Low-Entangled Ultrahigh Molecular Weight Polyethylene: Analytical Model and Computer Simulations, Macromolecules (Washington, DC, U. S.) 53 (2020) 6796–6808. https://doi.org/10.1021/acs.macromol.0c01077.
- [24] R.P. Gote, D. Mandal, K. Patel, K. Chaudhuri, C.P. Vinod, A.K. Lele, S.H. Chikkali, Judicious Reduction of Supported Ti Catalyst Enables Access to Disentangled Ultrahigh Molecular Weight Polyethylene, Macromolecules (Washington, DC, U. S.) 51 (2018) 4541–4552. https://doi.org/10.1021/acs.macromol.8b00590.
- [25] Z. Yue, N. Wang, Y.u. Cao, W. Li, C.-D. Dong, Reduced Entanglement Density of Ultrahigh-Molecular-Weight Polyethylene Favored by the Isolated Immobilization on the MgCl 2 (110) Plane, Ind. Eng. Chem. Res. 59 (8) (2020) 3351–3358, https:// doi.org/10.1021/acs.iecr.9b06780.
- [26] P. Chen, H. Yang, T. Chen, W. Li, Weakly Entangled Ultrahigh Molecular Weight Polyethylene Prepared via Ethylene Extrusion Polymerization, Ind. Eng. Chem. Res. 54 (44) (2015) 11024–11032, https://doi.org/10.1021/acs.iecr.5b03059.
- [27] D. Romano, N. Tops, E. Andablo-Reyes, S. Ronca, S. Rastogi, Influence of Polymerization Conditions on Melting Kinetics of Low Entangled UHMWPE and Its Implications on Mechanical Properties, Macromolecules (Washington, DC, U. S.) 47 (2014) 4750–4760. https://doi.org/10.1021/ma5008122.
- [28] F.P. Wimmer, V. Ebel, F. Schmidt, S. Mecking, Compartmentalized polymerization in aqueous and organic media to low-entangled ultra high molecular weight polyethylene, Polym. Chem. 12 (21) (2021) 3116–3123, https://doi.org/10.1039/ D1PY00394A.
- [29] S. Rastogi, L. Kurelec, J. Cuijpers, D. Lippits, M. Wimmer, P.J. Lemstra, Disentangled State in Polymer Melts; a Route to Ultimate Physical and Mechanical Properties, Macromol. Mater. Eng. 288 (12) (2003) 964–970, https://doi.org/ 10.1002/mame.200300113.
- [30] H. Xu, C.-Y. Guo, Polymerization in the confinement of molecular sieves: Facile preparation of high performance polyethylene, Eur. Polym. J. 65 (2015) 15–32, https://doi.org/10.1016/j.eurpolymj.2014.11.037.
- [31] P. Kenyon, S. Mecking, Pentafluorosulfanyl Substituents in Polymerization Catalysis, J. Am. Chem. Soc. 139 (39) (2017) 13786–13790, https://doi.org/ 10.1021/jacs.7b06745.
- [32] W. Li, T. Chen, C. Guan, D. Gong, J. Mu, Z.-R. Chen, Q.i. Zhou, Influence of Polyhedral Oligomeric Silsesquioxane Structure on the Disentangled State of Ultrahigh Molecular Weight Polyethylene Nanocomposites during Ethylene in Situ Polymerization, Ind. Eng. Chem. Res. 54 (5) (2015) 1478–1486, https://doi.org/ 10.1021/ie504273r.
- [33] W. Li, C. Guan, J. Xu, Z.-R. Chen, B. Jiang, J. Wang, Y. Yang, Bimodal/Broad Polyethylene Prepared in a Disentangled State, Ind. Eng. Chem. Res. 53 (3) (2014) 1088–1096, https://doi.org/10.1021/ie403315v.
- [34] W. Li, H. Yang, M. Shang, T. Chen, W. Wang, Structural and Morphological Evolution of Nascent Polyethylene during Ethylene in Situ Polymerization within Fe 3 O 4 @SiO 2 Nanoparticles, Ind. Eng. Chem. Res. 55 (32) (2016) 8719–8725, https://doi.org/10.1021/acs.iecr.6b01312.
- [35] R. Bärenwald, S. Goerlitz, R. Godehardt, A. Osichow, Q. Tong, M. Krumova, S. Mecking, K. Saalwächter, Local Flips and Chain Motion in Polyethylene Crystallites: A Comparison of Melt-Crystallized Samples, Reactor Powders, and Nanocrystals, Macromolecules (Washington, DC, U. S.) 47 (2014) 5163–5173. https://doi.org/10.1021/ma500691k.
- [36] P. Chammingkwan, Y. Bando, L.T.T. Mai, T. Wada, A. Thakur, M. Terano, L. Sinthusai, T. Taniike, Less Entangled Ultrahigh-Molecular-Weight Polyethylene Produced by Nano-Dispersed Ziegler-Natta Catalyst, Ind. Eng. Chem. Res. 60 (7) (2021) 2818–2827, https://doi.org/10.1021/acs.iecr.0c05432.
- [37] R. Huang, C.E. Koning, J.C. Chadwick, Synergetic Effect of a Nickel Diimine in Ethylene Polymerization with Immobilized Fe-, Cr-, and Ti-Based Catalysts on MgCl 2 Supports, Macromolecules (Washington, DC, U. S.) 40 (2007) 3021–3029. https://doi.org/10.1021/ma070071j.
- [38] R. Hoff, Handbook of Transition Metal Polymerization Catalysts, secondnd ed., John Wiley & Sons Incorporated, Newark, 2018.
- [39] M. Chen, Y. Chen, W. Li, P. Liang, C. Ren, B. Jiang, J. Wang, Y. Yang, Synthesis of Weakly Entangled Ultra-High-Molecular-Weight Polyethylene with a Fine Particle Size, Ind. Eng. Chem. Res. 60 (8) (2021) 3354–3362, https://doi.org/10.1021/acs. iecr.0c05838.
- [40] W. Zhang, W.-H. Sun, C. Redshaw, Tailoring iron complexes for ethylene oligomerization and/or polymerization, Dalton Trans. 42 (25) (2013) 8988–8997, https://doi.org/10.1039/C2DT32337K.
- [41] Y. Champouret, O.H. Hashmi, M. Visseaux, Discrete iron-based complexes: Applications in homogeneous coordination-insertion polymerization catalysis, Coord. Chem. Rev. 390 (2019) 127–170, https://doi.org/10.1016/j. ccr.2019.03.015.
- [42] V.A. Zakharov, N.V. Semikolenova, T.B. Mikenas, A.A. Barabanov, G.D. Bukatov, I. G. Echevskaya, M.A. Mats'ko, Homogeneous and supported catalysts based on bis (imino)pyridyl Iron(II) complexes for ethylene polymerization, Kinet Catal 47 (2006) 303–309. https://doi.org/10.1134/S0023158406020236.
- [43] A.A. Barabanov, G.D. Bukatov, V.A. Zakharov, N.V. Semikolenova, T.B. Mikenas, I. G. Echevskaja, M.A. Matsko, Kinetic Study of Ethylene Polymerization Over Supported Bis(imino)pyridine Iron (II) Catalysts, Macromol. Chem. Phys. 207 (15) (2006) 1368–1375, https://doi.org/10.1002/macp.200600122.
- [44] R. Huang, N. Kukalyekar, C.E. Koning, J.C. Chadwick, Immobilization and activation of 2,6-bis(imino)pyridyl Fe, Cr and V precatalysts using a MgCl2/AlRn (OEt)3–n support: Effects on polyethylene molecular weight and molecular weight
Y.L. Wencke et al.

distribution, J. Mol. Catal. A: Chem. 260 (1-2) (2006) 135-143, https://doi.org/10.1016/j.molcata.2006.07.030.

- [45] S. Ray, S. Sivaram, Silica-supported bis(imino)pyridyl iron(II) catalyst: nature of the support-catalyst interactions, Polym. Int. 55 (8) (2006) 854–861, https://doi. org/10.1002/pi.2020.
- [46] N.V. Semikolenova, V.N. Panchenko, E.A. Paukshtis, M.A. Matsko, V.A. Zakharov, Study of supported catalysts, prepared via binding of Fe(II) bis(imino)pyridyl complex with silica, modified by alumina: Effect of surface Lewis acidic sites on catalyst composition and activity in ethylene polymerization, Mol. Catal. 486 (2020) 110878, https://doi.org/10.1016/j.mcat.2020.110878.
- [47] E. Bauer (Ed.), Iron Catalysis II, Springer International Publishing, Cham, 2015.
 [48] S.B. Cordeiro, M.d.F.V. Marques, Evaluation of Bis(imino)pyridine Iron Catalyst on
- Heterogeneous Ethylene Polymerization, Ch&Cht 14 (2) (2020) 185–194.
 [49] H. Liu, E.M. Troisi, J.G.P. Goossens, J.R. Severn, C.W.M. Bastiaansen, Rheological properties of bimodal polyethylenes produced with silica nanoparticle supported catalysts, J. Appl. Polym. Sci. 136 (21) (2019) 47577, https://doi.org/10.1002/
- app.v136.2110.1002/app.47577.
 [50] N. Kukalyekar, L. Balzano, G.W.M. Peters, S. Rastogi, J.C. Chadwick, Characteristics of Bimodal Polyethylene Prepared via Co-Immobilization of Chromium and Iron Catalysts on an MgCl 2 -Based Support, Macromol. React. Eng.
- 3 (8) (2009) 448–454, https://doi.org/10.1002/mren.200900021.
 [51] H.-W. Shen, B.-H. Xie, W. Yang, M.-B. Yang, Thermal and rheological properties of polyethylene blends with bimodal molecular weight distribution, J Appl Polym Sci 129 (4) (2013) 2145–2151, https://doi.org/10.1002/app.v129.410.1002/
- [52] J.R. Severn, J.C. Chadwick, Tailor-Made Polymers, Wiley, 2008.
- [53] H.L. Wagner, The Mark–Houwink–Sakurada Equation for the Viscosity of Linear Polyethylene, J. Phys. Chem. Ref. Data 14 (2) (1985) 611–617, https://doi.org/ 10.1063/1.555751.
- [54] M. Spronck, A. Klein, B. Blom, D. Romano, Synthesis of Disentangled Ultra-High Molecular Weight Polyethylene using Vanadium(V)-Based Catalysts, Z. Anorg. Alle, Chem. 644 (17) (2018) 993–998. https://doi.org/10.1002/zaac.201800165.
- Allg. Chem. 644 (17) (2018) 993–998, https://doi.org/10.1002/zaac.201800165.
 [55] J.S. Evenson, Y.L. Wencke, G.A. Luinstra, C. Emmelmann, in: B. Müller (Ed.), Fraunhofer Direct Digital Manufacturing Conference DDMC 2020: Conference Proceedings, March 2020, Berlin, Germany, Fraunhofer Verlag, Stuttgart, 2020.
- [56] S. Kotha, V.R. Shah, Design and Synthesis of 1-Benzazepine Derivatives by Strategic Utilization of Suzuki-Miyaura Cross-Coupling, Aza-Claisen Rearrangement and Ring-Closing Metathesis, Eur. J. Org. Chem. 2008 (6) (2008) 1054–1064, https://doi.org/10.1002/ejoc.200700921.
- [57] E.M. Schoeneberger, G.A. Luinstra, Investigations on the Ethylene Polymerization with Bisarylimine Pyridine Iron (BIP) Catalysts, Catalysts 11 (2021) 407, https:// doi.org/10.3390/catal11030407.
- [58] C. Görl, H.G. Alt, Iron complexes with ω-alkenyl substituted bis(arylimino)pyridine ligands as catalyst precursors for the oligomerization and polymerization of ethylene, J. Mol. Catal. A: Chem. 273 (1-2) (2007) 118–132, https://doi.org/ 10.1016/j.molcata.2007.04.001.
- [59] V.C. Gibson, G.A. Solan, Olefin Oligomerizations and Polymerizations Catalyzed by Iron and Cobalt Complexes Bearing Bis(imino)pyridine Ligands, in: R.M. Bullock (Ed.), Catalysis without Precious Metals, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2010, pp. 111–141.
- [60] Z. Yang, J. Shi, X. Pan, B. Liu, X. He, Effects of different ultrahigh molecular weight polyethylene contents on the formation and evolution of hierarchical crystal structure of high-density polyethylene/ultrahigh molecular weight polyethylene blend fibers, J. Polym. Sci. 58 (16) (2020) 2278–2291, https://doi.org/10.1002/ pol.20200205.
- [61] F. Zhong, R. Thomann, R. Mülhaupt, Tailoring Mono-, Bi-, and Trimodal Molar Mass Distributions and All-Hydrocarbon Composites by Ethylene Polymerization

European Polymer Journal 163 (2022) 110936

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on Bis(imino)pyridine Chromium(III) Supported on Ultrathin Gibbsite Single Crystal Nanoplatelets, Macromolecules (Washington, DC, U. S.) 52 (2019) 2701–2711. https://doi.org/10.1021/acs.macromol.9b00091.

- [62] A.E. Ferreira, M.L. Cerrada, E. Perez, V. Lorenzo, E. Valles, J. Ressia, H. Cramail, J. P. Lourenco, M.R. Ribeiro, UHMWPE/HDPE in-reactor blends, prepared by in situ polymerization: Synthetic aspects and characterization, Express Polym. Lett. 11 (2017) 344–361. https://doi.org/10.3144/expresspolymlett.2017.34.
- [63] A. Valente, A. Mortreux, M. Visseaux, P. Zinck, Coordinative chain transfer polymerization, Chem. Rev. 113 (5) (2013) 3836–3857, https://doi.org/10.1021/ cr300289z.
- [64] M. Seitz, W. Milius, H.G. Alt, Iron(II) coordination compounds with ω-alkenyl substituted bis(imino)pyridine ligands: Self-immobilizing catalysts for the polymerization of ethylene, J. Mol. Catal. A: Chem. 261 (2) (2007) 246–253, https://doi.org/10.1016/j.molcata.2006.07.078.
- [65] H. Alshammari, H.G. Alt, Transition Metal Complexes of Allylated α-Diimines as Self-Immobilizing Catalysts for the Polymerization of Ethylene, JJC 9 (2014) 34–49, https://doi.org/10.12816/0026393.
- [66] H.G. Alt, C. Grl, Self-Immobilizing Catalysts for Olefin Polymerization, in: J. R. Severn, J.C. Chadwick (Eds.), Tailor-Made Polymers, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim, Germany, 2008, pp. 305–326.
- [67] Z. Wang, G.A. Solan, W. Zhang, W.-H. Sun, Carbocyclic-fused N, N, N-pincer ligands as ring-strain adjustable supports for iron and cobalt catalysts in ethylene oligo-/polymerization, Coord. Chem. Rev. 363 (2018) 92–108, https://doi.org/ 10.1016/j.ccr.2018.02.016.
- [68] M. Chen, Y. Chen, W. Li, C. Dong, P. Liang, N. Wang, B. Jiang, J. Wang, Y. Yang, Selective distribution and contribution of nickel based pre-catalyst in the multisite catalyst for the synthesis of desirable bimodal polyethylene, Eur. Polym. J. 135 (2020), 109878, https://doi.org/10.1016/j.eurpolymj.2020.109878.
- [69] H. Liu, C.W.M. Bastiaansen, J.G.P. Goossens, A.P.H.J. Schenning, J.R. Severn, Bimodal Ultrahigh Molecular Weight Polyethylenes Produced from Supported Catalysts: The Challenge of Using a Combined Catalyst System, Macromol. Chem. Phys. 218 (2017) 1600490, https://doi.org/10.1002/macp.201600490.
- [70] B. Wunderlich, Thermal Analysis of Polymeric Materials, Springer-Verlag Berlin Heidelberg, Berlin, Heidelberg, 2005.
- [71] S. Rastogi, Y. Yao, S. Ronca, J. Bos, J. van der Eem, Unprecedented High-Modulus High-Strength Tapes and Films of Ultrahigh Molecular Weight Polyethylene via Solvent-Free Route, Macromolecules (Washington, DC, U. S.) 44 (2011) 5558–5568. https://doi.org/10.1021/ma200667m.
- [72] Rastogi, Kurelec, Lemstra, Chain Mobility in Polymer Systems: On the Borderline between Solid and Melt. 2. Crystal Size Influence in Phase Transition and Sintering of Ultrahigh Molecular Weight Polyethylene via the Mobile Hexagonal Phase, Macromolecules (Washington, DC, U. S.) 31 (1998) 5022–5031. https://doi.org/ 10.1021/ma980261h.
- [73] L. Fang, Y. Leng, P. Gao, Processing and mechanical properties of HA/UHMWPE nanocomposites, Biomaterials 27 (2006) 3701–3707, https://doi.org/10.1016/j. biomaterials.2006.02.023.
- [74] A. Bistolfi, M.B. Turell, Y.-L. Lee, A. Bellare, Tensile and tribological properties of high-crystallinity radiation crosslinked UHMWPE, J. Biomed. Mater. Res. B Appl. Biomater. 90 (2009) 137–144, https://doi.org/10.1002/jbm.b.31265.
- [75] R. Hosseinnezhad, S. Talebi, M. Rezaei, The unique effect of chain entanglements and particle morphology on the sintering of ultrahigh molecular weight polyethylene, J. Elastomers Plast. 49 (2017) 609–629, https://doi.org/10.1177/ 0095244316681833.
- [76] M. Schmid, Laser sintering with plastics: Technology, processes, and materials, Carl Hanser Verlag, Munich, 2018.

4.3 HDPE@UHMWPE Powders for Power Bed Fusion Based Additive Manufacturing

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4.3.1 Synopsis and aim of this research

The strategy of this research consisted of the usage of commercial UHMWPE powders as convenient template for the production of polymer-on-polymer core shell particles with the intention of the shell acting as adhesive in the PBF process (Figure 30). This approach could potentially be used as a drop-in technology to widen the application profile of commercially available UHMWPE powders towards the PBF process.

The lower melt viscosity of HDPE could possibly enhance the formation of entanglement in the sintering process between the shell and the core as well as with neighboring particles. This would subsequently lead to a much higher adhesion between the particles and a mechanically sounder build part. Ideally, only a thin layer of HDPE needs to be synthesized on top of the UHMWPE particle to generate these effects.



Figure 30: Strategy for the formation of polymer-on-UHMWPE core shell particles

The first step of this strategy was to coat commercial UHMWPE particles with nano-sized silica particles in a high energy mixing process. The next step was the catalyst impregnation with a BIP iron (II) catalyst and the subsequent HDPE shell formation by polymerization. The results from 4.1 in terms of the activation strategy were successfully employed.

The results of these investigations were published in the following publication.

RESEARCH ARTICLE



HDPE@UHMWPE Powders for Power Bed Fusion Based Additive Manufacturing

Yannick L. Wencke, Friedrich Proes, Phillip Imgrund, and Gerrit A. Luinstra*

Commercial UHMWPE powder of 60 µm size (d50) embossed with 2–5 wt% of nanosilica is used as a support for the preparation of core-shell HDPE@silica@UHMWPE particles. The HDPE shell is generated by polymerization of ethylene in toluene slurry after treatment of the silica@UHMWPE with a methyl aluminoxane activated bisimine pyridine iron complex. Heat pressing the powder gives a solid material with identifiable original UHMWPE particles and a layer from fusion of UHMWPE and the surrounding HDPE shell; the properties match those of the UHMWPE base material. The powder flow properties of the HDPE@silica@UHMWPE are insufficient for a powder bed fusion process, a value for the flow function between 2 and 3 is measured in a ring shear tester. Additivation with nanosilica helps to overcome the insufficient flowability and allows the material to be recoated in a power bed fusion system. Laser sintering gives evidence for a substantial mixing and welding of the HDPE shells and UHMWPE. Caking at the surface of the built parts hinders the manufacturing of isolated parts. Further additivation with carbon black reduces the caking; however, the welding within the HDPE@silica@UHMWPE material is much less strong.

1. Introduction

The powder bed fusion technology (PBF) in the context of the art of additive manufacturing (AM) with polymer powders is probably the most versatile method of preparing thermoplastic 3D objects with a property profile close to that of the bulk material.^[1–3] The requirements on powder and materials for selective laser sintering (SLS or powder bed fusion/laser beam w/ polymers:

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PBF-LB/P) in a bed are derived from the manipulation of the powder in the equipment, the melting by laser light, the rheology of the melt and solidification/crystallization of the material.^[4] Triads of printability resp. of printed parts have been introduced to arrange the multiple, mutually dependent factors that need matching.^[2] Next to the powder properties, the material property profile limits the properties of the built part (mechanics, accuracy of the CAD model imaging, internal stress, distortion etc.).^[4,5]

Control over temperature in SLS and suitable thermal properties of the polymer are of highest importance for a satisfactory welding result. A sinter window, i.e., a region of a supercooling between melting and crystallization temperature larger than about 10 K should favorably exist for a particular polymer powder usable in PBF-LB/P. The bed temperature is set in the sinter window. Sintering in the supercooling region should prevent or at least minimize intermediate crystallization that can lead to curling.^[6] The heated powder of the bed is

molten by laser irradiation allowing the material to flow and contact neighboring entities. Initially, a so-called necking between the powder particles starts the fusing process to the built part.^[7] A solidification and a densification after a coalescence in the molten state must occur to obtain solid parts. Crystallization should occur in a controlled, uniform process during cooling of the bed, otherwise it may result in local tensions by nonuniform shrinkage and effectively to distorted parts.^[8–10] A too low amount of molten material may result in a freezing at the necking stage and will lead to porous parts.^[11] Low melt viscosities and low surface tensions of the melt will enhance wetting ability of the melt. These, in combination with the drivers in form of large surface area of the molten particles and capillary forces between the particles favor the full fusion of the powder. Viscoelastic forces on the other hand will oppose the flow of material.

Residual air between the particles and in the particles needs to exit from the molten material for a void free part. Consequently, it is easier to produce a solid part from dense particles and a powder with a high packing density.^[12] The present best practice commercial PBF-LB/P polyamide-12 powder has an optimum at an average particle diameter in the range of 45–90 μ m with less than 5% fines (relating to particles of radius in the range of about 10% of the median of the distribution) for good flowability and a sphericity larger than 0.6.

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Decoration with SiO_2 Gatalyst impregnation and polymerization <math>HDPE HDPE HDPE

Scheme 1. Route to HDPE@silica@UHMWPE core-shell-shell particles.

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The technology of PBF-LB/P thus relies on the availability of suitable polymer powders.^[13,14] Far most commercially available powders are obtained from bulk materials.^[1] Various technologies are available for reaching powders of miscellaneous constitutions in terms of sizes, distribution and shapes.^[15] These include solvent precipitation,^[16] (cryogenic) milling,^[17,18] and fiber cutting^[19] also in combination with rounding^[20,21] and sieving, coextrusion with a sacrificial polymer or spray drying.^[22,25]

Arriving at a suitable powder is not trivial and constitutes a barrier for the development of the AM technology. Commercially offered polymeric materials for PBF-LB/P are mainly polyamides.^[26] Others such as thermoplastic polyurethanes or polyetherketones have a substantially smaller share,[13] and the large-scale commodity polyethylenes and polypropylenes only find niche application.[27] The processing of polyethylenes in SLS appears mainly to have been used for the preparation of porous parts.^[28-31] In cases with other targets, warping and curling have led to severe distortions. The polyolefines however offer low cost and a broad property profile, useful in many every day applications.^[32] Blends of PE with ultrahigh molecular weight polyethylene (UHMWPE) gives materials with an even extended property profile,^[33] but the high melt viscosity limits the processability in any procedure.[34] UHMWPE parts produced by PBF-LB/P from commercially available sources cannot compete with traditionally produced parts in terms of material properties.[35-38] The printed parts from UHMWPE often have a lower mechanical stability and dimensional accuracy (warpage and curling). The overall material property profile, in particular also for medical applications,^[39] however, is very attractive and developing a suitable UHMWPE grade for processing by PBF-LB/P seems rewarding. The preparation of various UHMWPEs and its blends by transition metal synthesis is also still progressing, and a development of a grade for 3D printing seems timely.^[40-45]

The aim of this study is to provide advanced UHMWPE composite powders with the option to prepare superior UHMWPE parts by laser sintering. A facile route to UHMWPE built parts seemed to use core-shell particles in form of HDPE@UHMWPE as starting point. The highly entangled core would contribute most of the mass and lead to good mechanics, whereas the shell would bring all the properties needed for an effective fusion by SLS. The molten shell thus should have a low viscosity to ease fusion of the particles, and at the same time have a tendency to entangle with the surface segments of the core. Commercial UHMWPE particles were chosen as a core; the shell was prepared by polymerizing ethylene onto its surface. The in situ ethylene polymerization was made possible by using an activated homogeneous catalyst in form of the BIP (bisimine pyridine) iron dichloride complexes (BIP-FeCl₂) in combination with aluminum alkyls. The catalyst was supported onto nanosilica particles that were embossed beforehand into the surface of the designated core (**Scheme 1**).

2. Results and Discussion

2.1. Modifying UHMWPE as Template for SLS

The choice of UHMWPE was dictated by the particle size of the commercial UHMWPE powders available (Table S1, Supporting Information). The CELANESE product GUR 4150-3 with an average particle size $(x_{50.3})$ of 60 $\mu{\rm m}$ (d50) was chosen for the core. This leaves enough space to form a shell before leaving the suitable range for PBF-LB at a maximum of about 120 µm. Precipitated silica was selected as a catalyst nanosupport over other inorganic materials, such as alumina or magnesium dichloride particles, as a robust carrier for ethylene polymerization catalysts with high (nano)porosity ensuing high surface area.^[46–48] Nanoparticulate silica was thus contacted with UHMWPE in a dual asymmetric centrifuge with a load ranging from 2 to 5 wt%, leading to the surface decoration of the polyethylene particles (dry mixing). This method of high impact was used prior to bind carbon particles to a polymer powder matrix.[49] The size of the projection of the silica spheres always surmounts the surface of the GUR 4150-3 particles in the theoretical case of perfect smooth surface of the UHMWPE particles. This allows to substantially decorate the actual rough surface and or parts of the subsurface. The SEM analysis showed that the UHMWPE particles had also undergone ain the context of PBF-favorable general compacting and rounding of their shape (Figure S1, Supporting Information). Also, and unfavorably, the formation of some UHMWPE/silica particle debris is observed at higher silica loadings of 5 wt%. A subsequent separation of the particle mixture with the goal of removing particle debris or undecorated, loose silica was not performed in this initial effort to keep the procedure simple. Most of the mass is unaffected. The GUR-4150-3 shows partially cracked particles and parts may be present that are sensitive to mechanical pressure.[50]

The silica@UHMWPE support was subsequently activated for the polymerization of ethylene by fixation of a bisimine pyridine

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Figure 1. Exemplary SEM images of HPDE@silica5@UHWMPE core-shell particles. A) Overview of the particles at 250×. B) Single particle overview at 2500×. C) Overview over the surface of a particle at 10 000×. D) Closeup of the particle surface at 25 000×. Reaction conditions: 8 μ mol L⁻¹ of 1 activated with 0.84 mL of 1.7 mmol L⁻¹ MAO on 1 g of silica (5 wt%) embossed into UHMWPE, 20 °C, 3 bars of ethylene, 200 RPM, 600 mL of toluene with 9 × 10⁻³ M of TEA, 15 min of polymerization time.

iron complex and a cocatalyst. A fixation of a catalyst can be performed by several procedures.^[51] The interaction between catalyst support and catalyst can be complex and lead to a plethora of different effects.[46,52] It was found effective for reaching an active polymerization system with N,N'-(2,6-pyridinediyl diethylidyne) bis[2,6-diethyl-benzenamine] iron dichloride 1 (Scheme 1) to activate it in toluene solution with methyl aluminoxane MAO and subsequently add the silica@UHMWPE particle powder. The parent BIP FeCl₂ complex is very little soluble in toluene, but the activated cation-anion ensemble is molecularly dissolved, allowing to distribute the compound over the embedded silica particles. The polarity of the cation-anion complex will lead to an adsorption onto the silica.^[45] After removing the toluene solvent, the activated catalyst is tentatively finely dispersed on the surface of the silica@UHMWPE particles. Complex 1 leads to a catalyst that yields HDPE in a range of 10-100 kDa.[33,34] This was initially considered a suitable component to form a processable blend with UHMWPE.[33]

Formation of the shell from ethylene was reached by addition of the silica@UHMWPE particles coated with the activated catalyst to a reactor containing toluene saturated with ethylene. The toluene phase also had a 9×10^{-3} M concentration of triethyl aluminum (TEA). Latter compound reacts with complex 1 and its products after MAO treatment to make it virtually inactive for polyethylene formation, either through coordination to the active site or by formation of soluble paraffins and alkenes by chain transfer processes.^[54] Thus, any catalyst derived from 1 dissociating from the silica tends to become inactive for HDPE formation



Figure 2. Particle size density distributions for core-shell particles with varying amounts of silica on the surface. Reaction conditions: see caption of Figure 1.

in solution. It is thus found that most of the HDPE was homogeneously formed on the immobilized silica@UHMWPE.

SEM analysis revealed the formation of individual, replicates of the core UHMWPE particles (Figure 1). The synthesized coreshell particles showed a distinct shift of the particle size to larger diameters (d50 of \approx 60 µm up to \approx 70 µm; Figure 2; Table S2,

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Figure 3. SEM images of HDPE@UHMWPE core-shell particles with 2 wt% of silica. Reaction conditions: 8 μ mol L× 10⁻³ M of 1 activated with 0.84 mL of 1.7 mmol L⁻¹ MAO on 1 g of silica coated on UHMWPE, 20 °C, 3 bars of ethylene, 200 RPM, 600 mL of toluene containing 9 × 10⁻³ M of TEA, 15 min of polymerization time.

Supporting Information). The distribution is a copy of the starting UHMWPE along with a shoulder of varying intensity toward smaller sizes. This shoulder fraction always makes up a small part of the total mass, but is more intense at higher loadings of the nanosilica catalyst support. The shell growth is comparable for the various loads of silica particles up to 4 wt%.

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The maximum of the distribution function of the resulting HDPE@silica5@UHMWPE (the number after "@silica" will relate to the content in wt% relative to UHMWPE) is appreciable lower than for lower loadings. This may have several causes, most likely the higher content of silica on debris picking up more catalyst and hence giving more PE formation in that range of sizes. It was therefore decided to use silica4@UHMWPE (4 wt% of silica on UHMWPE) as the support with the highest useful silica loading.

The surface roughness is somewhat higher than the smoothened surfaces of the silica coated UHMWPE particles after higher energy mixing (Figure S1, Supporting Information). Core-shell particles obtained from precursor silica@UHMWPE with loadings of 2 and 3 wt% showed a more irregular shell than those with a higher silica content. The particles with the lower silica content and thus overall catalyst loadings show spots with more extensive polymer growth, leading to mushroom type of shapes (Figure 3). Silica particles may have been partly expulsed from the UHMWPE by the formation of HDPE. Also, the interlayer pressure that builds up when polyethylene is formed between the catalyst support and UHMWPE may lead to this type of separation.^[35] Such a process may also possibly be the main source for the smaller particles in the distribution (vide supra). A higher concentration of ethylene would lead to a more extensive shell formation around the silica nanoparticles. Higher loadings of silica at the surface give a stronger competition for ethylene, generally leading to a more balanced local growth and even shell, potentially also after partly expulsion of the more active/more loosely bound silica particles (Figure 3 and Figure S2, Supporting Information). The loading of about 4 wt% of silica gave the best result with respect to the amount of debris/fines and surface smoothness. This material was used in PBF-LB/P screening tests and is denoted as HDPE@silica4@UHMWPE. The HDPE shell on the UHMWPE was substantially connected to the core. Neither delamination nor breaking of shell or core of the particles could be detected after cryomilling or sonification (Figure S3, Supporting Information).

The HDPE content increases fast in the early stages of the polymerization and then reaches a more or less constant value. A content of 36 wt% is found after 15 min of reaction time at a constant pressure of 3 bars of ethylene. The reactions are performed in a semibatch mode, a mass flow controller admitting the equivalent to any consumed ethylene. The maximum rate of ethylene uptake is reached after about 30 min of reaction time, at a 55 wt% HDPE shell around the UHMWPE core. Either the catalyst had deactivated, or and more likely, a diffusion barrier the growing HDPE shell effectively inhibits ethylene reaching the catalyst.^[36,37]

The size of the particles increases accordingly with the reaction time. The median particle size ($x_{50.3}$) increased from 67.5 \pm 0.5 µm after a reaction time of 15 min to 83.0 \pm 1.7 µm at 60 min (vide infra). The $x_{50.3}$ value of the particles prepared at longer polymerization times had a larger spread. This may be the result of the development of the morphology to a more course cauliflower type of surface (**Figure 4**). It is expected that particles with such a morphology have substandard flow properties and will have a lower bulk particle density.^[55] The polymerization time was therefore set at 15 min for the larger scale preparation of HDPE@silica4@UHMWPE in this orientating study.

A ten-fold increase of scale led to comparable products of HDPE@silica4@UHMWPE, giving quantities of over 300 g per batch. The procedure of adding the activated catalyst on the UHMWPE support as toluene slurry was adapted to accommodate the larger volumes involved. The UHMWPE particles decorated with the activated catalyst were now added as slurry in toluene to the reactor in a counter flow of nitrogen gas. The toluene solvent in the reactor had prior been saturated with ethylene at 3 bars. The pressure was released to ambient pressure and the ethylene feed was exchanged for nitrogen, but dissolved ethylene was not removed. Upon complete addition of the particles, the reactor was pressurized again with ethylene to 3 bars. This method was prior tested in the screening reactor to have little effect on the outcome of the particle properties (Figure S4, Supporting Information).

The experiments in the 10 L equipment were reproducible, but gave overall lower HDPE content (22 wt% vs 36 wt%) and a 4– 5 µm smaller median particle size. This effect results most likely

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Figure 4. SEM images of HDPE@silica4@UHMWPE core-shell particles after a reaction time of 60 min. Reaction conditions: 8 μ mol L⁻¹ of 1 activated with 0.84 mL of 1.7 mmol L⁻¹ MAO on 1 g of silica coated on UHMWPE, 20 °C, 3 bars of ethylene, 200 RPM, 600 mL of toluene containing 9 mmol L⁻¹ of TEA, 60 min of reaction time.



Figure 5. SEM images of HDPE@silica4@UHMWPE core-shell particles from a 10 L reactor. Reaction conditions: 8 μ mol L⁻¹ 1 activated with 8.4 mL of 1.7 mmol L⁻¹ MAO on 10 g of 4 wt% silica coated on UHMWPE, 20 °C, 3 bars of ethylene, 200 RPM, 6 L of toluene containing 9 × 10⁻³ M of TEA, 15 min of reaction time.

from the procedure, i.e., to the lower steady state concentration of ethylene in the 10 L reactor. A mass transport barrier exists as ethylene is added over the gas phase, the surface-to-volume ratio being smaller in the larger equipment. The morphology of the resulting particles was comparable to the screening scale results, also more showing a finer cauliflower type of surface. This apparently represents an earlier stage of a more even shell formation (**Figure 5**). Although an optimization (ongoing research) is possible, it was decided to progress with the obtained particles as they were in a suitable range for PBF-LB and have a relatively fine structured surface. It is used in the PBF experiments.

2.2. Thermal Processing of the HDPE@silica@UHMWPE Particles

The core-shell @UHMWPE particles are a new type of PE composites.^[33] Objects prepared from it by thermal-mechanical processing (heat pressing and injection molding) behave as expected for a part from a HDPE composite highly filled with UHMWPE.^[58] The type of processing has a large influence on the mechanical properties. Heat pressing the GUR 4150-3 and the derived powders to plates allowed to prepare testing bars by diecutting. The thermal sintering procedure has a certain relevance to laser sintering as the particles also are not significantly displaced from their position before fusion. Although the pressure

 Table 1. Mechanical properties of processed HDPE@silica4@UHMWPE

 and UHMWPE.

	E _{mod} [MPa]	Yield strength [MPa]	Ultimate tensile stress [MPa]	Elongation at break [%]
GUR 4150-3 sintered	148 ± 38	17 ± 1	44 ± 9	492 ± 64
HDPE@UHMWPE sintered ^{a)}	174 ± 26	20 ± 1	32 ± 4	489 ± 60
HDPE@UHMWPE injection molded ^{b)}	232 ± 60	29 ± 6	29 ± 6	26 ± 5

^{a)} Shell makes up 48 wt% HDPE; ^{b)} Shell makes up 36 wt%.

is higher and the processing time is longer in the heat pressing, a laser heated melt may have higher local temperatures, which would allow a faster processing.

The mechanical properties were mapped from tensile testing (Table 1) on DIN ISO 527 type 5B samples. The stressstrain behavior is of a standard crystalline thermoplastic material with strain hardening (Figure S5, Supporting Information). Heat-pressed HDPE@silica5@UHMWPE generally shows an extended property profile over the commercial UHMWPE product, except for the ultimate tensile strength. The data show that by sintering an all-polyethylene solid part is accessible from the composite particles with useful mechanical properties.^[59]



Figure 6. HDPE and silica content in semibatch reactions with different reaction times with 1 heterogenized on 1 g of silica (4 wt%) coated on UHMWPE (left) and the resulting median particle diameter (right). Reaction conditions: 8 µmol L⁻¹ 1 activated with 0.84 mL of 1.7 mmol L⁻¹ MAO on 1 g of 4 wt% silica coated on UHMWPE, 20 °C, 3 bars of ethylene, 200 RPM, 600 mL of toluene containing 9 \times 10⁻³ M of TEA, 15–60 min of reaction time.

The importance of the HDPE shell on the mechanical properties of the resulting build part several samples with different amounts of HDPE in the shell was evaluated after an injection molding process. The respective samples were prepared by varying the polymerization time (Figure 6). The injection molding gives composite polyethylenes with a much lower elongation at break (Table 1; Figure S6, Supporting Information). Latter decreases with the HDPE content from 27% at 36 wt% HDPE shell to 17%-15% at a HDPE shell content of 55%-59%. The elastic modulus is somewhat higher than that of thermally sintered samples, but the tensile strength and elongation at break remain far short of the heat-pressed samples.

Melt mixing HDPE and UHMWPE generally does not easily lead to a homogenous blend.[60-62] The interactions between the UHMWPE polymer chains, which are not particularly sheared from the particle surface to a major extent in the standard extruder process, are smaller than in pressed samples.^[63] The time for disentangling and mixing of the polyethylenes is smaller than in heat pressing, and effectively little interface is formed. This holds true also for the HDPE@silica4@UHMWPE arrangement and is more extensive at a higher HDPE content. The mechanical properties then resemble that of a filled HDPE of low-to-medium molecular weight.

Cryo-fractured testing bars from injection molding show the basically unchanged original UHMWPE particles in a matrix of HDPE (Figure S7, Supporting Information). The cryo-break showed a clean break through the matrix and the particles. No distinct holes of pulled out particles were visible, indicating some load transfer over the HDPE-UHMWPE interface, but not nearly as much as in the sintered samples.^[64] The nanosilica particles are readily observable in the HDPE matrix, some remain at the interface between to UHMWPE. This may indicate that the silica particles are partly loosened from the surface in the shell forming process. It also gives evidence, that the catalyst indeed is (majorly) associated with the nanosilica particles.

2.3. Powder Properties of HDPE@silica@UHMWPE

The composite HDPE@silica4@UHMWPE has a small sinter window of 11 K, just short of that of the parent UHMWPE (≈15 K) and a HDPE@silica (12 K) prepared from 1 supported

Table 2. Thermal properties of the polyethylene powders.

Reaction time [min]

Material	T _{melting} onset [°C]	T _{crystallization} onset [°C]	Sinter window [°C]
GUR 4150-3	130.5	115.7	14.8
HDPE@silica4@UHMWPE	129.9	118.9	11.0
HDPE@silica ^{a)}	130.6	118.2	12.5

^{a)} Prepared without the embossing process from catalyst 1 supported onto nanosilica.

on nanosilica, and ethylene). The sinter window was determined between the first onset of melting and the first onset of crystallization (Table 2). The introduction of silica into the thermoplastic matrix usually creates additional nucleation sites for the crystallization process during the cooling cycle.^[65] This may result the observed higher crystallization temperatures of the samples with silica used.

Such a small window comprises a challenge in PBF-LB/P for preventing premature crystallization as the bed temperature needs to be quite high (closer to the melting point), and solidification after laser melting is subsequently slower.^[2] The synthesized HDPE@UHMWPE powders basically have the same sphericity of 0.88 (±0.01) as the parent UHMWPE powder (Table S3, Supporting Information). This holds true also for the silica-treated UHMWPE powders before polymerization. The different surface morphologies of the HDPE@silica#@UHMWPE (# = 2-4) particles are not mirrored in the results of the particle sphericity analysis. Neither the silica content on the surface of the UHMWPE particles nor the polymerization reaction time has an impact on the outcome of the particle sphericity measurement outcome.

The bulk densities of the synthesized HDPE@silica#@UHMWPE materials with various amounts of silica (2-4 wt%) dial in roughly at 60% of the parent UHMWPE material (Figure 7). The powders were also subjected to high energy mixing with the objective to improve the flowability and to increase the bulk density. The high impact forces in the dual asymmetric centrifuge mixing process leads to a thermoplastic deformation of the polymer surface, smoothening it on the micrometer scale and reducing possible bridges between particles and protuberances on the particle surface. Flow agents in the

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as synthesized

after high energy mixing

Figure 7. Bulk densities and flow function of HDPE@UHWMPE with various silica coating on the UHMWPE (left) and of HDPE@silica4@UHMWPE particles (right).

form of nanosized silica were employed in the same mixing step to distribute these over the surface of the particles. This leads to an increased flowability by reducing the interparticle forces by generating a nanorough surface. Applying the high energy mixing process to these samples brings the bulk density to almost the value of parent UHMWPE (at 80%–95%).

The flowability of the powders was estimated from measurements of the ffc value in a ring shear tester. The particle flow functions of the HDPE@silica#@UHMWPE (# of 2–4) particles from the reactor were low (20% to 10%) in comparison to the parent UHMWPE (ffc of 5) and to a PA12 PBF reference (ffc of 9.94). The pressure at which the ring shear tester operated was set to the lowest possible value (500 Pa) to mimic the operating conditions of the powder recoater in an SLS machine as closely as possible.

HDPE@silica4@UHMWPE particles have the highest fcc values after synthesis, in concert to the absence of protuberances. The ffc values show some scattering with the HDPE shell mass, but generally outrange the ffc of the particles with smaller silica loadings. The variations in fcc will results from the usual factors, like surface morphology and shape, next to the presence of debris. These will vary to some extent per batch (Figures 4 and 5).

High energy mixing substantially increased the flow function values for composites with 2 and 3 wt% silica, presumably because of a major smoothing (approximately at micrometer dimension) of the surface. The impact of high energy mixing of HDPE@silica4@UHMWPE on the ffc value is appreciable lower. The higher values of the flow function for these types of composites are hardly changing and/or even deteriorate by the impact. This may indicate that a surface smoothness improvement is only small. The positive effect of mechanical impact on the ffc is possibly overridden by the action of some formed debris/fines, increasing the friction between the particles. This matter will need further clarification in the future.

The ffc values of 2-3 of the particles were too low for a useful operation in PBF. A standard post-synthesis additivation was therefore carried out to improve the flowability. The addition of round, solid nanosilica particles were shown to be a good choice as they act as spacers between the particles and decrease the interparticle forces.[66] Ideally, the lowest possible content of silica is used to generate a useful flowability; any amount of silica will act as a filler, lowering the toughness of the polymer built part. Unfortunately, no increase in flowability could be observed after the addition of low contents (0.1, 0.25, 0.5 wt%) to HDPE@silica4@UHMWPE. This may result from the nanoparticles filling cracks/voids and indentions at the particles surface, and not acting as spacer. Addition of higher amounts of silica (2.5 and 5 wt%) were tested too and do lead to the intended increase in flowability, even to an ffc value of about 11 at a content of 2.5 wt% nanosilica (Figure 8) was reached. Latter concentration of silica is not favorable to the built part property profile.

The HDPE@silica4@UHMWPE samples with different amounts of flow additive were subsequently tested for recoating in an adapted EOS P390 in the range of 120–125 °C. The flowability is also dependent on the temperature. For example, it is known to increase with temperatures for PA12 as residual moisture is evaporated.^[67] Consistent to the expectation, no recoating with HDPE@silica4@UHMWPE powders could be



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Figure 8. Flow functions of HDPE@silica4@UHMWPE powders with various amounts of added nanosilica flow additive.

achieved in the absence of nanosilica. In contrast, efficient recoating could be observed for samples containing as low as 0.75 wt% of nanosilica. It was decided to additivate the HDPE@ silica4@UHMWPE powders at high mixing energy with 1 wt% of nanosilica. In a subsequent stage, additionally 0.25 wt% of carbon black CB was added to counteract caking by laser light scattering and to enhance local absorption.

2.4. PBF-LB/P with HDPE@silica4@UHMWPE

An initial parameter set for the PBF-LB/P process with HDPE@silica4@UHMWPE, additivated with 1 wt% nanosilica and alternatively with 1 wt% silica combined with 0.25 wt% CB, was obtained in a small study, limited by the available quantity of composite powder.

Therefore, the bed temperature, the laser power, scan speed and scan line distance and number of exposures were varied in an adapted building chamber of an EOS P390 (Figure S8, Supporting Information). A statistically relevant set could not be obtained, rather the momentary best possible settings (best practice) were elaborated. In this, the layer thickness of the powder was set to 120 μ m, a standard value and compatible with the low content of particles larger in diameter. The best setting point for the laser related parameter were found by starting at low energy densities and subsequently increasing the latter. This procedure is economic in the use of the limited amount of powder.

Screening of the temperature dependence of the recoatability with non-additivated HDPE@silica4@UHMWPE resulted in the choice of 122.5 °C for the bed temperature. It seemed the highest acceptable temperature, above this temperature, clumping at some spots in the bed was unavoidable due to the intermittent activated IR lamps, leading to a destruction of the even layer (Figure S9, Supporting Information). The laser energy was incrementally increased until mechanically connected powders were obtained in case of HDPE@silica4@UHMWPE particles with 1 wt% nanosilica.

No parameter set was identified with the limited amount of powder of this initial study for receiving isolable testing bars. The



result was that the built tensile test specimens were enclosed by larger amounts of adhered or partially sintered powder (Figure S10, Supporting Information, top), or very brittle objects were obtained. Note that the settings are not based on a representative parameter screening study for the PBF-LB/P process. The objective was to achieve a first impression on the prospects for building a solid part along the route. The resulting built part from the exposed powder was then evaluated for melt flow, voids, warping/curling, and/or other defects.

An analysis of the fusion process by SEM images of cryofractured material at the building and the fracture surface shows that the UHMWPE in HDPE@silica4@UHMWPE with only nanosilica additivation had been partially molten. A substantial flow and welding of powder was achieved. The fracture is not along the UHMWPE core particle surface, but a transfer of load to the UHMWPE "filler" during fracture had taken place (**Figure 9**, left). This is reminiscent of the results of building parts by heat pressing, hinting that some HDPE and UHMWPE merger has taken place.^[G8]

The top surface of the sintered specimens appears smooth (Figure S11, Supporting Information), showing that the melting had led to a thorough fusion. Close up views show that some voids are present with flow aid nanosilica sticking out of the surface (Figure 9, right). Adjacent to the lasered area, powder with necking contacts and powder adhering to the lasered area are detected (Figure S11, Supporting Information middle). The laser energy was dispersed into the bed with a completely caked bed as result. Nevertheless, the welding has the perspective of being superior to the thermal pressing of the powder as the UHMWPE tends to fuse more intensely with HDPE than in injection molding (Figure S7, Supporting Information). The conditions for laser sintering on the other hand were not very suitable for welding the nanosilica additivated compound into a 3D printed part.

Further experiments with variation of bed temperature and laser power were not undertaken with the limited resource of powder. Rather, to reduce the caking by scattered laser light, the HDPE@silica4@UHMWPE particles were additivated with additionally 0.25 wt of CB as optical absorber, i.e., next to 1 wt% of nanosilica. This led to substantially fused particles to a solid, however, isolation of built parts from the created block was still not possible (Figure S10, Supporting Information). The caking was nevertheless greatly reduced by the additional additivation of HDPE@silica4@UHMWPE/nanosilica mixture with CB. The melt surface was smooth but interspersed with holes (Figure 10). Layers of molten material with sintered material in between could be observed in the side view of the cryo-fractured sample. This was an indicator for insufficient laser light penetration through a recoated layer of particles during the laser light exposure. A close-up of the molten areas showed ball and socket failure. Possibly, the laser energy absorption was merely at the shell where the carbon black is located. Thus, not enough thermal energy was reaching the UHMWPE cores to melt them (Figure 10). This is comparable to a situation of injection molding with a comparable result where there is again insufficient energy available to melt/entangle the UHMWPE cores (Figure S7, Supporting Information).

The same additivation with nanosilica and CB and PBF-LB/P procedure was used to prepare testing bars from commercial UHMWPE as a point of reference for the sintering procedure.



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Figure 9. SEM images HDPE@silica4@UHMWPE with 1 wt% of nanosilica built by PBF. Left: fracture surface, right: top view of the lasered area.



Figure 10. SEM images of the cryo-fractured tensile test specimens (top) and its top surface (bottom) of HDPE@silica4@UHMWPE with 1 wt% of nanosilica and 0.25 wt% of CB built by PBF.

The result again was a solid block of fused tasting bars (Figure S10, Supporting Information, bottom). The cross section again showed insufficient interlayer melting (Figure S12, Supporting Information). The molten layers were even much less dense with voids as the matrix HDPE is missing. The main failure mode was also between neck sintered and barely molten particles. The top surface of this tensile test specimen mirrored this observation as it consisted of neck molten particles. No smooth polymer melt had formed. The HDPE@silica4@UHMWPE particles thus show a superior behavior, and have a higher potential as a source for PBF-LB/P to prepare well-fused parts. The results also indicate that it is useful to optimize the particles along with the laser sintering procedure. This is currently in progress.

3. Conclusions

HDPE@UHMWPE core-shell particles with particle size distributions under 200 µm and thus suitable for powder bed fusion additive manufacturing were prepared using a versatile approach. Commercial powder UHMWPE particles were embossed with commercial nanosilica in a dual asymmetric centrifuge. An easily accessible BIP iron catalyst was activated by the universal activator MAO, and subsequently supported onto the silica by a simple solvent contact. The resulting particles have a limited flowability, but a standard additivation with nanosilica allows a PBF recoater to handle it. Laser sintering the HDPE@silica@UHMWPE gives evidence for a mixing of the shell and core polyethylenes, concomitant with the promise of

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obtaining superior built parts (relative to HDPE). It will, however, be necessary to increase the absorption of laser light by in situ additivation to reach a deeper welding and stop caking from deflected laser energy. As the action of BIP iron catalysts in the sense of the type of polyethylene formation can easily tuned by variation in the ligand^[66,69,70] or mixtures of BIP catalyst could be used to get to blends of diverse polyethylenes,^[33] we think the new procedure established in this work offers the possibility to generate a new class of all-polyethylene composites tailor-made for powder based additive manufacturing.

4. Experimental Section

Materials: All manipulation of air- and/or moisture-sensitive compounds was carried out under a dry nitrogen atmosphere using standard Schlenk techniques. UHMWPE GUR 4150-3 was a gift from Celanese Corporation. Ketjenblack EC 300] was obtained from Weber und Schaer, Hamburg, Hamburg, Germany. Perkasil 300 KS was generously supplied by W. R. Grace and Company. Silicon dioxide nanoparticles (20-60 nm) were obtained from Ionic Liquids Technologies GmbH, Heilbronn, Baden-Württemberg, Germany (they appear as solid, mostly round particles). Synthesis of 2,6-bis[1-(2,6-diethylphenyl-imino)ethyl-ene]pyridine iron(II) dichloride 1 was based on a literature report.[71] Nitrogen was obtained from Praxair Deutschland GmbH and used as purchased. Toluene was obtained from Merck and purified by distillation and passing through columns filled with molecular sieve (4 Å) and BASF catalyst R3-11/G. Ethylene was obtained from Westfalen AG and was purified by passing through columns filled with molecular sieve (4 Å) and BASF catalyst R3-11/G. MAO was obtained from Crompton as a 10 wt% solution in toluene and used as received. Triethyl aluminum was purchased as a 25 wt% solution in toluene from Sigma-Aldrich and used as received.

Adapted EOS P390 for PBF Testing: A reduced building chamber had been built at the Fraunhofer IAPT.^[72] Several issues were addressed such as correlating the setpoint temperature and the actual temperature on the powder surface, adjusting the gap distance between parts so no powder leakages occur and insulating as well as heating of the build chamber. The optimization strategy of the PBF process was executed as follows: The starting temperature was chosen at the low end (120 °C) of the sintering window and efficient recoating was tested for several layers (Figure S9, Supporting Information) at the chosen temperature after the machine reached a thermal equilibrium. Subsequently, the first laser exposures were tested with a low laser power setting. Ideally, the lowest amount of laser energy is needed to sufficiently melt the material. This minimizes the risk of melting outside of the wanted geometry, as well as minimizing the risk of burning the material. The resulting exposed powder was evaluated for warping or curling. If no dimensional deviation was observed and the recoating process could continue without any disturbances the build job was finished. The built parts were then manually assessed for its mechanical stability. This process was repeated until a set of parameters was reached where the polymer in the laser track is consolidated and dimensionally stable. Empirical found best practice parameters were: laser power 36 W; layer thickness 0.24 mm; scan speed 1500 mm s⁻¹; scanline distance 0.3 mm; energy density 1.33 J mm⁻³; exposure speed mm² s⁻¹; single exposure.

DSC Measurements: Melting and crystallization of the polymer composites was investigated using a DSC1 of the company Mettler Toledo (Columbus, OH). Standard non-isothermal crystallization experiments were executed for all sample compositions by heating from 25 to 250 °C at a rate of 10 K min⁻¹. The sample was held at 250 °C for 5 min and then cooled to 25 °C with a cooling rate of 10 K min⁻¹. After holding the sample at this temperature, the sample was subjected to a second heating and cooling cycle with the same parameters as above. Experiments were executed under a nitrogen atmosphere.

Particle Size, Distribution, and Shape: Particle size and distribution of the polymer powders and composites were measured on a HELOS KR laser diffraction sensor equipped with a RODOS/GRADIS dry dispersion setup of the company Sympatec (Clausthal-Zellerfeld, Lower Saxony, GerMaterials and Engineering www.mame-journal.de

Table 3. Conditions of the preparation of $\mathsf{HDPE}@\mathsf{UHMWPE}$ core-shell particles.

Support	[g]	Toluene [mL]	Catalyst 1 [µmol]	MAO [mmol]	TEA [mmol]	Yield [g]	HDPE content [wt%]
silica2 @UHMWPE	50	600	4.8	1.44	5.4	67.88	26.3
silica3 @UHMWPE	33	600	4.8	1.44	5.4	52.64	37.3
silica4 @UHMWPE	25	600	4.8	1.44	5.4	39.35	36.5
silica5 @UHMWPE	20	600	4.8	1.44	5.4	38.64	48.2
silica4 @UHMWPE	250	6000	48	14.4	54	320.9	22.0

Notes: Reaction conditions: 20 °C, 3 bar of ethylene, 15 min, 200 RPM.

many). Particle roundness was determined by a dynamic image analysis according to ISO 13322-2 with a Camsizer XT of the company Retsch (Haan, North-Rhine-Westfalia, Germany).

Mechanical Measurements: Tensile test specimens of the type 5A (DIN EN ISO 527) were prepared by injection molding at 180 °C with 750 bars of pressure with a HAAKE Minijet II of the company Thermo Fischer Scientific (Waltham, MA). Heat sintering was performed in molds of 100 \times 100 \times 1 mm³. The powder was heated to 200 °C while applying a pressure of 200 bars. After 10 min of pressing, the mold was allowed to slowly cool to room temperature. Tensile test specimens derived from DIN EN ISO 527-5A were prepared from the plate by die cutting. Tensile testing was performed on a Zwicki-Line Z1.0 of the company ZwickRoell (Ulm, Baden-Württemberg, Germany) with 1 kN force transducer and a crosshead speed of 50 mm min⁻¹ and at 23 °C. Samples were kept at that temperature and under the exclusion of moisture prior to measurement.

SEM Imaging: Samples were coated with carbon using a Leica ACE 600 prior to analysis with a LEO 1525 Gemini scanning electron microscope (Wetzlar, Hesse, Germany). Micrographs were recorded at an acceleration voltage of 5 kV.

Powder Rheology: Powder flowability measurements were executed on a ring-shear-tester RST-XS.s of the company Dietmar Schulze (Wolfenbüttel, Lower Saxony, Germany). A sample of 20 g was placed inside the ring shear tester and subjected to a pressure of 500 Pa. Measurements were subsequently taken at 75 Pa intervals down to 200 Pa. Commercial PA12 PBF powder was measured to set a benchmark for further measurements. A bulk density of 498 kg m⁻³ and a flow function of 9.94 could be recorded. This corresponds well to the literature data.^[67]

Synthesis of HDPE@silica#@UHMWPE Core-Core-Shell Particles: Coating of polymer powders with silica for the purpose of catalyst immobilization was performed in a two-step process in a Speedmixer DAC 400.1 FVZ of the company Hauschild & Co KG. Silica of the type Perkasil 300 (W.R. Grace and Company) and the amount of GUR 4150-3 polymer powder were placed in a mixing container (PP 300, Hauschild & Co KG) at a scale of 100 g (x g of silica and 100-x g of polymer). The mixing container was subsequently cooled in an ice/water bath to ≈ 0 °C. The cooled container was subjected to mixing at 2500 rpm for 1 min. Upon completion of the mixing the container was cooled again in ice to ≈ 0 °C. This cycle was repeated five times.

Small-scale polymerization experiments (Table 3): Prior to the polymerization the 1 L steel reactors were heated for 10 min with a 650 °C heat gun from the inside before subjecting to a dynamic vacuum for at least one hour. Toluene (600 mL) was transferred to the evacuated reactor, which was subsequently filled with nitrogen up to 50 mbar overpressure. The toluene was conditioned at the reaction temperature of 20 °C, and subsequently saturated with ethylene at 3 bars of ethylene. Thereafter, the relevant amounts of TEA [9 × 10⁻³ M in the reactor, 2.87 mL (5.4 mmol) of

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25 wt% TEA in toluene] were added to the toluene using standard Schlenk techniques and a syringe.

An amount of silica@UHMWPE was dried in a Schlenk flask under a dynamic vacuum at 80 °C for 2.5 h. The amount of silica in silica@UHMWPE was always 1 g by calculation, e.g. for a synthesis with silica4@UHMWPE, 25 g of starting material were used. After cooling to ambient temperature, 50 mL of dry toluene were added. Next, 2 mL (4.8 µmol, 2.6 mg) of a dispersion of 2.4 µmol/mL of 1 in toluene, 0.84 mL (1.44 mmol) of MAO, Al/Fe 300, 3.5 mL of dry toluene were combined. This activated catalyst solution was added to the toluene dispersion of the silica@UHMWPE using a syringe. The silica@UHMWPE and catalyst solution were mixed using a laboratory vortex mixer. The solvents were finally removed in a dynamic vacuum for 60 min to receive a free-flowing beige powder.

The catalyst powder was subsequently dispersed in 50 mL of dry toluene and injected with a syringe into the prepared reactor, starting the polymerization reaction. After the desired reaction time (15, 30, 45, or 60 min), the excess ethylene was released, and the cocatalyst was quenched by the addition of small aliquots (5–20 mL) of ethanol. The resulting slurry was then mixed with \approx 1.5 L of ethanol and filtered. The white powder was dried at 40 °C under a dynamic vacuum overnight.

Large-scale polymerization experiments (Table 3): Larger scale reactions were carried in a 10 L steel reactor (Juchheim Laborgeräte GmbH, Bernkastel-Kues, Germany). Prior to the polymerization the 10 L steel reactor was heated for 10 min with a 650 °C heat gun from the inside before closing the lid and subjecting the inner part to dynamic vacuum overnight at 120 °C. Toluene (6000 mL) was placed inside the evacuated reactor, which was subsequently pressurized with nitrogen to 50 mbar overpressure. The toluene was saturated with ethylene at 3 bars of ethylene at room temperature. TEA [28.7 mL (54 mmol) of 25 wt% TEA in toluene] was added to the reactor using standard Schlenk techniques and a syringe.

Silica4@UHMWPE particles (250 g) were dried in a Schlenk flask under a dynamic vacuum at 80 °C for 2.5 h. After cooling to ambient temperature, 500 mL of dry toluene were added. In a Schlenk tube, 20 mL (48 µmol, 26 mg) of a dispersion of 2.4 µmol mL⁻¹ of 1 in toluene, 8.4 mL (14.4 mmol) of MAO, Al/Fe: 300, 35 mL of toluene were combined. This solution was transferred to the tube with the silica4@UHMWPE using a syringe. The silica4@UHMWPE and catalyst solution were shortly mixed using a laboratory vortex mixer. The solvents were removed in a dynamic vacuum for 4 h and a free-flowing beige powder was received. The powder was subsequently redispersed in 500 mL of dry toluene.

The ethylene pressure in the reactor was reduced to ambient pressure and the dispersed powder was injected. The ethylene pressure was readjusted to 3 bars. The pressure was kept constant using a mass flow controller. After 15 min of reaction time, the pressure was released, and the cocatalyst was quenched by the addition of small aliquots (50–200 mL) of ethanol. The resulting slurry was then mixed with \approx 15 L of ethanol and collected on a filter. The white powder was dried at 40 °C under a dynamic vacuum overnight. This adapted procedure does not change the outcome of the synthesis it was tested in the 1 L reactor (Figure S4, Supporting Information).

Additivation of UHMWPE and HDPE@silica#@UHMWPE Composite Particles: The commercially obtained or prepared UHMWPE particles were mixed with carbon black Ketjenblack EC 300J (Weber und Schaer, Hamburg, Hamburg, Germany) and with silicon dioxide nanoparticles (Ionic Liquids Technologies GmbH, Heilbronn, Baden Württemberg, Germany). Mixing was performed consecutively for each additive, using a Speedmixer DAC 400 (Hauschild & Co KG, Hamm, North Rhine-Westphalia, Germany) with a PP 300 mixing container (Hauschild & Co KG), switching between a cooling step, where the mixing container is cooled with ice water, and a mixing step with 2500 rpm for 1 min, for a total of five cycles for each additive (Table S4, Supporting Information).

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available in the Supporting Information of this article.

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- S. C. Ligon, R. Liska, J. Stampfl, M. Gurr, R. Mülhaupt, Chem. Rev. 2017, 117, 10212.
- [2] C. A. Chatham, T. E. Long, C. B. Williams, Prog. Polym. Sci. 2019, 93, 68.
- [3] R. Brighenti, M. P. Cosma, L. Marsavina, A. Spagnoli, M. Terzano, J. Mater. Sci. 2021, 56, 961,
- [4] M. Schmid, Laser Sintering with Plastics: Technology, Processes, and Materials, Carl Hanser Verlag, Munich 2018.
- [5] F. Lupone, E. Padovano, M. Pietroluongo, S. Giudice, O. Ostrovskaya, C. Badini, eXPRESS Polym. Lett. 2021, 15, 177,
- [6] J.-P. Kruth, P. Mercelis, J. Van Vaerenbergh, L. Froyen, M. Rombouts, Rapid Prototyping J. 2005, 11, 26,
- [7] C. T. Bellehumeur, M. Kontopoulou, J. Vlachopoulos, *Rheol. Acta.* 1998, 37, 270.
- [8] C. Nelson, Solid Freeform Fabr. Symp. Proc. 1995, 159.
- [9] P. Forderhase, M. McAlea, M. Michalewicz, M. Ganninger, K. Firestone, Solid Freeform Fabr. Symp. Proc. 1994, 102, 102.
- [10] P. Forderhase, M. Ganninger, K. McAlea, presented at Proc. 4th European Conf. Rapid Prototyping and Manufacturing, 1995.
- [11] R. Hosseinnezhad, S. Talebi, M. Rezaei, J. Elastomers Plast. 2017, 49, 609.
- [12] J.-P. Kruth, G. Levy, F. Klocke, T. H. C. Childs, CIRP Ann. 2007, 56, 730.
- [13] M. Schmid, A. Amado, K. Wegener, J. Mater. Res. 2014, 29, 1824.
- [14] L. J. Tan, W. Zhu, K. Zhou, Adv. Funct. Mater. 2020, 30, 2003062.
- [15] D. Drummer, M. Medina-Hernández, M. Drexler, K. Wudy, Proc. Eng. 2015, 102, 1918.
- [16] M. A. Dechet, J. Schmidt, Proc. CIRP 2020, 94, 95.
- [17] S. Xi, P. Zhang, Y. Huang, M. Kong, Q. Yang, G. Li, Polymer 2020, 186, 122044.
- [18] J. Schmidt, M. Sachs, C. Blümel, B. Winzer, F. Toni, K.-E. Wirth, W. Peukert, Proc. Eng. 2015, 102, 550.
- [19] J. Wulfhorst, G. Seide, T. Gries, D. Rietzel, D. Drummer, presented at 11th World Textile Conf. AUTEX, Mulhouse 2011.
- [20] P. Hejmady, L. C. A. Van Breemen, P. D. Anderson, R. Cardinaels, Powder Technol. 2021, 388, 401,

ADVANCED SCIENCE NEWS

www.advancedsciencenews.com

- [21] J. Schmidt, M. Sachs, S. Fanselow, M. Zhao, S. Romeis, D. Drummer, K.-E. Wirth, W. Peukert, *Chem. Eng. Sci.* 2016, http://doi.org/10.1016/ j.ces.2016.09.009
- [22] A. B. D. Nandiyanto, K. Okuyama, Adv. Powder Technol. 2011, http: //doi.org/10.1016/j.apt.2010.09.011
- [23] C. Eloo, M. Rechberger, in Produktgestaltung in der Partikeltechnologie (Ed: U. Teipel), Fraunhofer Verl, Stuttgart 2011, pp. 353–366.
- [24] M. S. Wahab, K. W. Dalgarno, R. F. Cochrane, S. H. Member, Lect. Notes Eng. Comput. Sci. 2009, 1499.
- [25] S. Yuan, F. Shen, C. K. Chua, K. Zhou, Prog. Polym. Sci. 2019, 91, 141.
- [26] A. J. Boydston, J. Cui, C.-U. Lee, B. E. Lynde, C. A. Schilling, ACS Macro Lett. 2020, 9, 1119.
- [27] A. Wegner, Phys. Proc. 2016, 83, 1003.
- [28] A. Siegmann, I. Raiter, M. Narkis, P. Eyerer, J. Mater. Sci. 1986, 21, 1180.
- [29] G. V. Salmoria, C. H. Ahrens, P. Klauss, R. A. Paggi, R. G. Oliveira, A. Lago, *Mater. Res.* 2007, *10*, 211.
- [30] J. Bai, B. Zhang, J. Song, G. Bi, P. Wang, J. Wei, Polym. Test. 2016, 52, 89.
- [31] L. Hao, M. M. Savalani, Y. Zhang, K. E. Tanner, R. A. Harris, Proc. IMechE 2006, 220, 125.
- [32] a) https://pcep.eu/polyolefin-applications (accessed: September 2021); b) Polyolefin Fibres: Industrial and Medical Applications (Ed: S. C. O. Ugbolue), Woodhead Publishing Ltd, Duxford 2017;
- [33] M. Stürzel, S. Mihan, R. Mülhaupt, Chem. Rev. 2016, 116, 1398.
- [34] S. Hambir, J. P. Jog, Bull. Mater. Sci. 2000, 23, 221.
- [35] Y. Khalil, A. Kowalski, N. Hopkinson, Manuf. Rev. 2016, 3, 15/1.
- [36] R. D. Goodridge, R. J. M. Hague, C. J. Tuck, J. Mater. Process. Technol. 2010, 210, 72.
- [37] J. T. Rimell, P. M. Marquis, J. Biomed. Mater. Res. 2000, 53, 414.
- [38] X. Zhu, Q. Yang, Plast., Rubber Compos. 2020, 49, 116.
- [39] UHMWPE Biomaterials Handbook: Ultra High Molecular Weight Polyethylene in Total Joint Replacement and Medical Devices (Eds: S. M. Kurtz), William Andrew an imprint of Elsevier, Amsterdam 2016.
- [40] K. Patel, S. H. Chikkali, S. Sivaram, Prog. Polym. Sci. 2020, 109, 101290.
- [41] A. Fiorentino, P. Panariti, L. Van Turnhout, M. Spronck, A. Klein, S. Schmitz, S. Rastogi, B. Blom, D. Romano, *Ind. Eng. Chem. Res.* 2020, 59, 12710.
- [42] F. P. Wimmer, V. Ebel, F. Schmidt, S. Mecking, Polym. Chem. 2021, 12, 3116.
- [43] J. Xia, Y. Zhang, S. Kou, Z. Jian, J. Catal. 2020, 390, 30.
- [44] P. Kenyon, S. Mecking, J. Am. Chem. Soc. 2017, 139, 13786.
- [45] J. R. Severn, in *Multimodal Polymers with Supported Catalysts* (Eds: A. R. Albunia, F. Prades, D. Jeremic), Springer International Publishing, Cham 2019, pp. 1–53.

- [46] G. G. Hlatky, Chem. Rev. 2000, 100, 1347.
- [47] J. R. Severn, J. C. Chadwick, Dalton Trans. 2013, 42, 8979.
- [48] M. A. Bashir, T. F. L. McKenna, in *Polymer Reaction Engineering of Dispersed Systems* (Ed: W. Pauer), Springer International Publishing, Cham 2018, pp. 19–63.
- [49] S. Forero, DE102010013210, 2010.
- [50] H. Zhang, S. Zhao, X. Yu, Z. Xin, C. Ye, Z. Li, J. Xia, J. Polym. Sci., Part B: Polym. Phys. 2019, 57, 632.
- [51] H. G. Alt, J. Chem. Soc., Dalton Trans. 1999, 1703.
- [52] L. L. Böhm, Macromol. Symp. 2001, 173, 53.
- [53] Z. Flisak, W.-H. Sun, ACS Catal. 2015, 5, 4713.
- [54] E. M. Schoeneberger, G. A. Luinstra, Catalysts 2021, 11, 407.
- [55] S. Zanoni, N. Nikolopoulos, A. Welle, A. Vantomme, B. M. Weckhuysen, Catal. Sci. Technol. 2021, 11, 5335.
- [56] M. Daftaribesheli Comparison of Catalytic Ethylene Polymerization in Slurry and Gas Phase, 2009.
- [57] T. F. Mckenna, J. B. P. Soares, Chem. Eng. Sci. 2001, 56, 3931.
- [58] a) Y.-M. Li, Y. Wang, L. Bai, H.-L.-Z. Zhou, W. Yang, M.-B. Yang, J. Macromol. Sci., Part B 2011, 50, 1249; b) H. S. Jaggi, B. K. Satapathy, A. R. Ray, J. Polym. Res. 2014, 27, 482; c) A. B. Boscoletto, R. Franco, M. Scapin, M. Tavan, Eur. Polym. J. 1997, 33, 97.
- [59] T. GmbH, https://u-hubs.com/wp-content/uploads/2019/10/GUR-PE-UHMW-Material-characteristics.pdf.
- [60] J. K. Keum, F. Zuo, B. S. Hsiao, Macromolecules 2008, 41, 4766.
- [61] Z. Zhai, C. Fusco, J. Morthomas, M. Perez, O. Lame, ACS Nano 2019, 13, 11310.
- [62] G. A. Schwartz, R. Bergman, J. Swenson, J. Chem. Phys. 2004, 120, 5736.
- [63] H. Shen, L. He, C. Fan, B. Xie, W. Yang, M. Yang, Polym. Eng. Sci. 2015, 55, 270.
- [64] J.-D. Zuo, Y.-M. Zhu, S.-M. Liu, Z.-J. Jiang, J.-Q. Zhao, Polym. Bull. 2007, 58, 711.
- [65] J. Rychly, I. Janigova, Thermochim. Acta 1993, 215, 211.
- [66] D. Schulze, http://site.ebrary.com/lib/alltitles/docDetail.action? docID=10203893.
- [67] D. Ruggi, C. Barrès, J.-Y. Charmeau, R. Fulchiron, D. Barletta, M. Poletto, Addit. Manuf. 2020, 33, 101143.
- [68] D. Hofmann, A. Kurek, R. Thomann, J. Schwabe, S. Mark, M. Enders, T. Hees, R. Mülhaupt, *Macromolecules* 2017, 50, 8129.
- [69] Z. Wang, G. A. Solan, W. Zhang, W.-H. Sun, Coord. Chem. Rev. 2018, 363, 92.
- [70] W. Zhang, W.-H. Sun, C. Redshaw, Dalton Trans. 2013, 42, 8988.
- [71] B. L. Small, M. Brookhart, A. M. A. Bennett, J. Am. Chem. Soc. 1998, 120, 4049.
- [72] J. S. Evenson, Y. L. Wencke, G. A. Luinstra, C. Emmelmann, in Fraunhofer Direct Digital Manufacturing Conference DDMC 2020 (Ed: B. Müller), Fraunhofer Verlag, Stuttgart 2020.

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5. Conclusion

The Investigations on the polymerizations of HDPE on spray dried silica revealed that particle growth is fast in earlier stages of the reaction and subsequent polymerization led to a densification of the polymer particle. To keep the silica content as low as possible and the yield as high as possible the optimal reaction should be executed at 3 bars of ethylene and a concentration of 8 mmol/L of precatalysts according to this screening of reaction parameters. The resulting particle size distribution of almost all reactions showed that the upper edge of the particle size distribution was bordering on the 200 µm mark previously set as maximal particle size for efficient PBF operation. To prevent creating even larger particles, lower temperatures (0-20 °C) and lower reaction times of one hour must be employed.

As these reaction conditions might only represent a local optimum, further research and parametrization needs to be directed towards increasing the powder density as well as smoothing the particle surfaces for better PBF suitability. Implementation of BIP-catalysts or catalyst mixtures (reactor blend technology) which are producing shorter chains might be of benefit. They might fill the "gaps" of the HDPE rough surfaces. To increase the direct suitability of the powder for PBF even more, laser absorbing species (carbon black, carbon nanotubes, molecular dyes) might be added to the catalyst supports. This research pointed out that the best results to prevent agglomeration can be achieved by "precipitating" the solvent swollen polymer particles after the reaction by exchanging the reaction solvent toluene with ethanol. Further research towards different solvents could be directed to find a suitable synthesis route. Ideally, overcritical carbon dioxide could be employed, mitigating the problem of surface tension agglomerating the particles.

The discovery of the ability of the newly developed BIP iron (II) catalyst to produce dUHMWPE led to the employment of this catalyst in the endeavor to generate PBF suitable powder based on dUHMWPE. This research showed the feasibility to use this catalyst together with the catalyst template effect to synthesize spherical particles in a useful size region for PBF. Full PBF suitability could not be reached due to the rough surface and resulting insufficient powder flowability of the powder. Nonetheless, first results in PBF experiments showed a melting and consolidation of the laser irradiated polymer i.e. a low viscous melt could be reached. These results are a promising starting point to generate true UHMWPE based parts by PBF. Future research should be aimed at smoothing the surface of the resulting powders and increasing the powder as well as the particle density and the laser absorptivity to increase the PBF suitability.

The research targeted at yielding HDPE@UHMWPE core-shell particles revealed that 4 wt% of silica added to the UHMWPE particles led to the optimal surface covering. Adding more

silica led to the formation of microparticles containing only silica as the surface of the UHMWPE particles could not absorb any more silica. Using less silica than 4 wt% led to an uneven coating of silica on the surface of the UHMWPE and subsequently to an uneven polymer shell formation. The resulting HDPE shells were mechanically intertwined with the UHMWPE cores. No delamination or breaking of the shell could be observed after cryo-milling or treatment with ultrasound. Reaction times longer than 15 minutes led to the formation of uneven shells and larger particles. The resulting mechanical properties of the bulk material corresponded to the properties of highly filled HDPE composites when processed by injection molding or press molding. Processing by PBF led to massive parts with SEM based evidence of mixing/entanglement between the HDPE shell and the UHMWPE core. This technology can serve as a crucial step towards the implementation of UHMWPE in PBF processes as it has several advantages: The bulk of the polymer powder can be synthesized by industrial scale processes while the shell can be fine-tuned by the application of different fillers and catalysts producing tailor-made polyethylenes. The employment of the core shell approach solves some of the problems encountered in the previous research: Using commercial UHMWPE particles as cores leads to higher powder densities needed for efficient PBF processing. The remaining challenges of increasing the powder smoothness, the powder flowability as well as the laser absorption remain the same. A unique challenge for this technique is the relatively high silica content in the final composite powder. A reduction in silica needed for a good surface covering of the UHMWPE cores and subsequent even surface covering of the resulting HDPE shell might even increase the mechanical properties of the built parts.

The PBF building showed that a fcc-value of 3 seemed to be sufficient to enable smooth recoater operation. Higher values guaranteed even smoother operation and should always be the target for future PBF powders based on these approaches. Building jobs with powders with a low bulk density gave porous and curled parts. Massive parts could be achieved with powders exhibiting bulk densities of 450 kg/m³ or higher The morphology of the polymer powder should be as round and smooth as possible to be able to flow well and to generate dense packings resulting in high bulk densities. Caking could be reduced, but not eliminated, by the employment of a laser absorbing additive. Increasing the laser absorption of the powder led to the increased phenomenon of lacking inter layer adhesion.

6. Bibliography

- (1) Gebhardt, A. Additive Fertigungsverfahren, 5th ed.; Hanser, 2016.
- (2) Ligon, S. C.; Liska, R.; Stampfl, J.; Gurr, M.; Mülhaupt, R. *Chem. Rev.* **2017**, *117* (15), 10212.
- (3) Schmid, M.; Amado, A.; Wegener, K. J. Mater. Res. 2014, 29 (17), 1824.
- (4) Kaddar, W. Die generative Fertigung mittels Laser-Sintern- Scanstrategien, Einflusse verschiedener Prozessparameter auf die mechanischen und optischen Eigenschaften beim LS von Thermoplasten und deren Nachbearbeitungsmoglichkeiten, University Duisburg-Essen, 2010.
- (5) Gibson, I.; Rosen, D. W.; Stucker, B. In *Additive Manufacturing Technologies*; Springer US: Boston, MA, 2010; pp 299–332.
- (6) Lee, C. S.; Kim, S. G.; Kim, H. J.; Ahn, S. H. J. Mater. Process. Technol. 2007, 187– 188, 627.
- (7) Goodridge, R. D.; Tuck, C. J.; Hague, R. J. M. Prog. Mater. Sci. 2012, 57 (2), 229.
- (8) Griehl, W.; Ruestem, D. Ind. Eng. Chem. 1970, 62 (3), 16.
- (9) Drummer, D.; Rietzel, D.; Kühnlein, F. *Phys. Procedia* **2010**, *5* (PART 2), 533.
- (10) Amado, A. Characterization and prediction of SLS processability of polymer powders with respect to powder flow and part warpage, ETH Zürich, 2016.
- (11) Kruth, J.; Mercelis, P.; Van Vaerenbergh, J.; Froyen, L.; Rombouts, M. *Rapid Prototyp. J.* **2005**, *11* (1), 26.
- (12) Kruth, J. P.; Levy, G.; Klocke, F.; Childs, T. H. C. CIRP Ann. Manuf. Technol. 2007, 56 (2), 730.
- (13) Schmid, M. Laser Sinter. with Plast. 2018, 101.
- (14) Amado, A.; Wegener, K.; Schmid, M.; Levy, G. In *5th International Polymers and Moulds Innovations Conference*; 2012; pp 207–216.
- (15) Nelson, J. C. Proc. Solid Free. Fabr. Symp. 1995, 159.
- (16) Forderhase, P.; McAlea, M.; Michalewicz, M.; Ganninger, M.; Firestone, K. Solid Free. *Fabr Symp Proc* **1994**, 102.
- (17) Forderhase, P.; Ganninger, M.; McAlea, K. *Proc. 4th Eur. Conf. Rapid Prototyp. Manuf.* **1995**.
- (18) Schmid, M. In Laser Sintering with Plastics; 2018; pp 39-64.
- (19) Amado, A.; Schmid, M.; Levy, G.; Wegener, K. In 22nd Annual International Solid Freeform Fabrication Symposium - An Additive Manufacturing Conference, SFF 2011; 2011; Vol. 12, pp 438–452.
- (20) Schulze, D. *Powders and Bulk Solids*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2007; Vol. 4.
- (21) Ruggi, D.; Barrès, C.; Charmeau, J. Y.; Fulchiron, R.; Barletta, D.; Poletto, M. *Addit. Manuf.* **2020**, 33 (July 2019), 101143.
- (22) Spierings, A. B.; Voegtlin, M.; Bauer, T.; Wegener, K. *Prog. Addit. Manuf.* **2015**, *1* (1–2), 9.
- (23) Schulze, D. *Pulver und Schüttgüter: Fließeigenschaften und Handhabung*, first edit.; Springer-Verlag: Berlin, 2009.

- (24) Schmid, M.; Amado, F.; Levy, G.; Wegener, K. In High Value Manufacturing: Proceedings of the 6th International Conference on Advanced Research in Virtual and Rapid Prototyping, Leiria, Portugal, 1-5 October, 2013; Taylor & Francis, 2014; pp 95– 99.
- (25) McGlinchey, D. Bulk Solids Handling: Equipment Selection and Operation; Wiley, 2009.
- (26) Krantz, M.; Zhang, H.; Zhu, J. Powder Technol. 2009, 194 (3), 239.
- (27) Leturia, M.; Benali, M.; Lagarde, S.; Ronga, I.; Saleh, K. *Powder Technol.* **2014**, 253, 406.
- (28) Freeman, R. Powder Technol. 2007, 174 (1-2), 25.
- (29) Vetterli, M.; Kleijnen, R.; Schmid, M.; Wegener, K. Antec 2018 2018, 2016.
- (30) Amado, A.; Schmid, M.; Wegener, K. *Flowability of SLS powders at elevated temperature*; Zürich, 2014.
- (31) Vock, S.; Klöden, B.; Kirchner, A.; Weißgärber, T.; Kieback, B. *Prog. Addit. Manuf.* **2019**, *4* (4), 383.
- (32) Koynov, S.; Glasser, B.; Muzzio, F. Powder Technol. 2015, 283, 103.
- (33) Yap, C. Y.; Chua, C. K.; Dong, Z. L.; Liu, Z. H.; Zhang, D. Q.; Loh, L. E.; Sing, S. L. *Appl. Phys. Rev.* **2015**, *2* (4).
- (34) Mamuschkin, V.; Roesner, A.; Aden, M. Phys. Procedia 2013, 41, 172.
- (35) Torrisi, L.; Caridi, F.; Visco, A. M.; Campo, N. Appl. Surf. Sci. 2011, 257 (7), 2567.
- (36) Ho, H. C. H.; Cheung, W. L.; Gibson, I. Rapid Prototyp. J. 2002, 8 (4), 233.
- (37) Masson, N. C.; Monteiro, V. A. R.; Souza, E. F. 1996; pp 267–279.
- (38) Bai, J.; Goodridge, R. D.; Hague, R. J. M.; Song, M. Polym. Eng. Sci. 2013, 53 (9), 1937.
- (39) Salmoria, G. V.; Paggi, R. A.; Lago, A.; Beal, V. E. Polym. Test. 2011, 30 (6), 611.
- (40) Yan, C.; Hao, L.; Xu, L.; Shi, Y. Compos. Sci. Technol. 2011, 71 (16), 1834.
- (41) Goodridge, R. D.; Shofner, M. L.; Hague, R. J. M.; McClelland, M.; Schlea, M. R.; Johnson, R. B.; Tuck, C. J. *Polym. Test.* **2011**, *30* (1), 94.
- (42) Bai, J.; Goodridge, R. D.; Yuan, S.; Zhou, K.; Chua, C. K.; Wei, J. *Molecules* 2015, 20 (10), 19041.
- (43) Yang, J.; Shi, Y.; Yan, C. J. Appl. Polym. Sci. 2010, 117 (4), 2196.
- (44) Childs, T. H. C.; Tontowi, A. E. *Proc. Inst. Mech. Eng. Part B J. Eng. Manuf.* **2001**, *215* (11), 1481.
- (45) Schultz, J. P.; Kander, M. R. G.; Suchicital, C. T. A. In *Solid Freeform Fabrication Symposium*; 2000; pp 119–124.
- (46) Drummer, D.; Medina-Hernández, M.; Drexler, M.; Wudy, K. *Procedia Eng.* **2015**, *102*, 1918.
- (47) Wahab, M. S.; Dalgarno, K. W.; Cochrane, R. F.; Member, S. H. Lect. Notes Eng. Comput. Sci. 2009, 2177 (1), 1499.
- (48) Schmidt, J.; Plata, M.; Tröger, S.; Peukert, W. Powder Technol. 2012, 228, 84.
- (49) Wulfhorst, J.; Seide, G.; Rietzel, D.; Drummer, D. In *11th World Textile Conference AUTEX*; 2011; pp 1–6.
- (50) Eloo, C.; Rechberger, M. Symp. Produktgestaltung der Partikeltechnologie **2011**, 353.

- (51) Thakare, Kavendra A Vishwakarma, Honeykumar G Bhave, A. G. Int. J. Res. Eng. Technol. 2015, 04 (12), 92.
- (52) Kerry, F. G. *Industrial gas handbook: Gas separation and purification*, first edit.; CRC Press: Boca Raton, 2007.
- (53) Jeremic, D. In Ullmann's Encyclopedia of Industrial Chemistry; 2014; pp 1–42.
- (54) Wencke, Y. L. Diblockcopolymeren zum Einsatz als Compatibilizer, University of Hamburg, 2016.
- (55) Richards, R. B. J. Appl. Chem. 2007, 1 (8), 370.
- (56) Stadler, F. J.; Piel, C.; Kaschta, J.; Rulhoff, S.; Kaminsky, W.; Münstedt, H. *Rheol. Acta* 2006, 45 (5), 755.
- (57) Münstedt, H. Soft Matter 2011, 7 (6), 2273.
- (58) de Gennes, P. G. J. Chem. Phys. **1971**, 55 (2), 572.
- (59) Pearson, D. S.; Helfand, E. *Macromolecules* **1984**, *17*(4), 888.
- (60) Ball, R. C.; McLeish, T. C. B. *Macromolecules* **1989**, *22* (4), 1911.
- (61) McLeish, T. C. B.; Milner, S. T. Adv. Polym. Sci. 1999, 143, 197.
- (62) Dingenouts, N.; Horvarth, A. *Praktikumsskript für das Polymerpraktikum des Karlsruher Institut für Technologie*; Karlsruhe, 2015.
- (63) Colby, R. H.; Rubinstein, M.; Viovy, J. L. *Macromolecules* **1992**, 25 (2), 996.
- (64) Kavassalis, T. A.; Noolandi, J. Phys. Rev. Lett. 1987, 59 (23), 2674.
- (65) Fetters, L. J.; Lohse, D. J.; Richter, D.; Witten, T. A.; Zirkel, A. *Macromolecules* **1994**, 27 (17), 4639.
- (66) Graessley, W. W.; Edwards, S. F. Polymer (Guildf). 1981, 22 (10), 1329.
- (67) Wu, S. J. Polym. Sci. Part B Polym. Phys. 1989, 27 (4), 723.
- (68) Stürzel, M.; Mihan, S.; Mülhaupt, R. Chemical Reviews. 2016, pp 1398–1433.
- (69) Lin, W.; Yang, Z.; Qu, J. Polym. Int. 2019, 68 (5), 904.
- (70) Mei, G.; Herben, P.; Cagnani, C.; Mazzucco, A. Macromol. Symp. 2006, 245–246, 677.
- (71) Stürzel, M.; Kurek, A. G.; Hees, T.; Thomann, Y.; Blattmann, H.; Mülhaupt, R. *Polymer* (*Guildf*). **2016**, *102*, 112.
- (72) Stürzel, M.; Hees, T.; Enders, M.; Thomann, Y.; Blattmann, H.; Mülhaupt, R. *Macromolecules* **2016**, *49* (21), 8048.
- (73) Stürzel, M.; Mihan, S.; Mülhaupt, R. Chem. Rev. 2016, 116 (3), 1398.
- (74) Chen, P.; Yang, H.; Chen, T.; Li, W. Ind. Eng. Chem. Res. 2015, 54 (44), 11024.
- (75) Li, W.; Guan, C.; Xu, J.; Chen, Z. R.; Jiang, B.; Wang, J.; Yang, Y. Ind. Eng. Chem. Res. 2014, 53 (3), 1088.
- (76) Flory, P. J. J. Am. Chem. Soc. 1936, 58 (10), 1877.
- (77) McNaught, A. D.; Wilkinson, A. In *IUPAC Compendium of Chemical Terminology*; Blackwell Scientific Publications: Oxford, 1997.
- (78) Koltzenburg, S.; Maskos, M.; Nuyken, O. *Polymer Chemistry*; Springer Berlin Heidelberg: Berlin, Heidelberg, 2017.
- (79) McNaught, A. D.; Wilkinson, A. In IUPAC Compendium of Chemical Terminology;

Blackwell Scientific Publications: Oxford, 1997.

- (80) Ravve, A. *Principles of Polymer Chemistry*, third.; Springer New York: New York, NY, 2012.
- (81) Fawcett, E. W. Trans. Faraday Soc. 1936, 32, 119.
- (82) Ronca, S. In *Brydson's Plastics Materials: Eighth Edition*; Elsevier Ltd, 2017; pp 247–278.
- (83) Roedel, M. J. J. Am. Chem. Soc. 1953, 75 (24), 6110.
- (84) Ehrlich, P.; Mortimer, G. A. In *Fortschritte der Hochpolymeren-Forschung*; Springer-Verlag: Berlin/Heidelberg, 1970; Vol. 7, pp 386–448.
- (85) Kehinde, A. J.; Usman, M. A.; Edoga, M. O.; Owolabi, R. U. Am. J. Polym. Sci. 2012, 2 (5), 91.
- (86) Bokis, C. P.; Ramanathan, S.; Franjione, J.; Buchelli, A.; Call, M. L.; Brown, A. L. *Ind. Eng. Chem. Res.* **2002**, *41* (5), 1017.
- (87) Mecking, S. Angew. Chemie **2001**, *113* (3), 550.
- (88) Förster, S.; Schnablegger, H.; Balsam, M.; Lach, C. *Nachrichten aus der Chemie* **2000**, *48* (3), 328.
- (89) Ziegler, K.; Krupp, F.; Zosel, K. Angew. Chemie 1955, 67 (16), 425.
- (90) Natta, G.; Corradini, P.; Allegra, G. J. Polym. Sci. 1961, 51 (156), 399.
- (91) Cossee, P. J. Catal. 1964, 3 (1), 80.
- (92) Böhm, L. L. Angew. Chemie Int. Ed. 2003, 42 (41), 5010.
- (93) Severn, J. R. In *Multimodal Polymers with Supported Catalysts*; 2019; pp 1–53.
- (94) Wilke, G. Angew. Chemie 2003, 115 (41), 5150.
- (95) Breslow, D. S.; Newburg, N. R. J. Am. Chem. Soc. 1957, 79 (18), 5072.
- (96) Natta, G.; Pino, P.; Mazzanti, G.; Giannini, U. J. Am. Chem. Soc. 1957, 79 (11), 2975.
- (97) Andresen, A.; Cordes, H.-G.; Herwig, J.; Kaminsky, W.; Merck, A.; Mottweiler, R.; Pein, J.; Sinn, H.; Vollmer, H.-J. *Angew. Chemie* **1976**, *88* (20), 689.
- (98) Chen, E. Y.-X.; Marks, T. J. Chem. Rev. 2000, 100 (4), 1391.
- (99) Wild, F. R. W. P.; Zsolnai, L.; Huttner, G.; Brintzinger, H. H. *J. Organomet. Chem.* **1982**, 232 (1), 233.
- (100) Bajgur, C. S.; Tikkanen, W. R.; Petersen, J. L. Inorg. Chem. 1985, 24 (16), 2539.
- (101) Hoffmann, R. Angew. Chemie Int. Ed. English 1982, 21 (10), 711.
- (102) Collins, R. A.; Russell, A. F.; Mountford, P. Appl. Petrochem. Res. 2015, 5, 153.
- (103) Keim, W. Angew. Chemie Int. Ed. 2013, 52 (48), 12492.
- (104) Ittel, S. D.; Johnson, L. K.; Brookhart, M. Chem. Rev. 2000, 100 (4), 1169.
- (105) Kempe, R. Chem. A Eur. J. 2007, 13 (10), 2764.
- (106) Valente, A.; Mortreux, A.; Visseaux, M.; Zinck, P. Chem. Rev. 2013, 113, 3836.
- (107) Baier, M. C.; Zuideveld, M. a.; Mecking, S. Angew. Chemie 2014, 126 (37), 9878.
- (108) Mazzolini, J.; Espinosa, E.; D'Agosto, F.; Boisson, C. Polym. Chem. 2010, 1 (6), 793.
- (109) Britovsek, G. J. P.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; McTavish, S. J.;

Solan, G. a.; White, A. J. P.; Williams, D. J. Chem. Commun. 1998, 311 (1), 849.

- (110) Britovsek, G. J. P.; Bruce, M.; Gibson, V. C.; Kimberley, B. S.; Maddox, P. J.; Mastroianni, S.; McTavish, S. J.; Redshaw, C.; Solan, G. a; Stroemberg, S.; White, A. J. P.; Williams, D. J. *J. Am. Chem. Soc.* **1999**, *121* (38), 8728.
- (111) Small, B. L.; Brookhart, M. J. Am. Chem. Soc. 1998, 120 (28), 7143.
- (112) Small, B. L.; Brookhart, M.; Bennett, A. M. a. J. Am. Chem. Soc. 1998, 120 (16), 4049.
- (113) Small, B. L. Acc. Chem. Res. 2015, 48 (9), 2599.
- (114) Meyer, R. S. a. Darstellung und Untersuchung von 2,6-Bis[1-(phenylimino)ethyl]pyridin-Eisen-(II)-Komplexen für die katalysierte Aufbaureaktion, University of Hamburg, 2009.
- (115) Meyer, R. Herstellung von maßgeschneidertem terminal-funktionalisiertem Polyethylen mittels der katalysierten Aufbaureaktion, University of Hamburg, 2013.
- (116) Scholtyssek, J. Katalysierte Synthese langkettiger Alkylverbindungen, University of Hamburg, 2008.
- (117) Scholtyssek, J. Entwicklung einer dreistufigen in-situ Synthese von Polyethylen / Silica-Nanocomposites, University of Hamburg, 2012.
- (118) Meyer, R. S. A.; Scholtyssek, J. S.; Luinstra, G. A. *Macromol. Mater. Eng.* 2015, 300 (2), 218.
- (119) Boudier, A.; Breuil, P.-A. R.; Magna, L.; Olivier-Bourbigou, H.; Braunstein, P. *Chem. Commun.* **2014**, *50* (12), 1398.
- (120) Alyea, E. C.; Merrell, P. H. Synth. React. Inorg. Met. Chem. 1974, 4 (6), 535.
- (121) Bouwkamp, M. W.; Bart, S. C.; Hawrelak, E. J.; Trovitch, R. J.; Lobkovsky, E.; Chirik, P. J. Chem. Commun. 2005, No. 27, 3406.
- (122) Bryliakov, K. P.; Talsi, E. P.; Semikolenova, N. V.; Zakharov, V. a. Organometallics **2009**, *28* (11), 3225.
- (123) Semikolenova, N. V.; Zakharov, V. A.; Echevskaja, L. G.; Matsko, M. A.; Bryliakov, K. P.; Talsi, E. P. *Catal. Today* **2009**, *144* (3–4), 334.
- (124) Bryliakov, K. P.; Semikolenova, N. V.; Zakharov, V. A.; Talsi, E. P. Organometallics **2004**, 23 (22), 5375.
- (125) Görl, C.; Beck, N.; Kleiber, K.; Alt, H. G. J. Mol. Catal. A Chem. 2012, 352, 110.
- (126) Görl, C.; Englmann, T.; Alt, H. G. Appl. Catal. A Gen. 2011, 403 (1-2), 25.
- (127) Bryliakov, K. P.; Semikolenova, N. V.; Zudin, V. N.; Zakharov, V. A.; Talsi, E. P. *Catal. Commun.* **2004**, *5* (1), 45.
- (128) Flisak, Z.; Sun, W. H. ACS Catal. 2015, 5 (8), 4713.
- (129) Tomov, A. K.; Gibson, V. C.; Britovsek, G. J. P.; Long, R. J.; Van Meurs, M.; Jones, D. J.; Tellmann, K. P.; Chirinos, J. J. *Organometallics* **2009**, *28* (24), 7033.
- (130) Kawakami, T.; Ito, S.; Nozaki, K. Dalt. Trans. 2015, 20745.
- (131) Small, B. L.; Brookhart, M. J. Am. Chem. Soc. 1998, 120 (28), 7143.
- (132) Schmidt, R.; Welch, M. B.; Palackal, S. J.; Alt, H. G. J. Mol. Catal. A Chem. 2002, 179 (1–2), 155.
- (133) Chen, Y.; Qian, C.; Sun, J. Organometallics 2003, 22 (14), 1231.
- (134) Gibson, V. C.; Spitzmesser, S. K. Chem. Rev. 2003, 103 (1), 283.
- (135) Gai, J.-G.; Zuo, Y. J. Mol. Model. 2012, 18 (6), 2501.

- (136) Vega, J. F.; Rastogi, S.; Peters, G. W. M.; Meijer, H. E. H. *J. Rheol. (N. Y. N. Y).* **2004**, *48* (3), 663.
- (137) Ahmad, M.; Wahit, M. U.; Abdul Kadir, M. R.; Mohd Dahlan, K. Z. *Sci. World J.* **2012**, *2012*, 1.
- (138) Hambir, S.; Jog, J. P. Bull. Mater. Sci. 2000, 23 (3), 221.
- (139) Kurtz, S. M. UHMWPE Biomaterials Handbook: Ultra High Molecular Weight Polyethylene in Total Joint Replacement and Medical Devices; Elsevier/Academic Press, 2015.
- (140) Sui, G.; Zhong, W. H.; Ren, X.; Wang, X. Q.; Yang, X. P. *Mater. Chem. Phys.* **2009**, *115* (1), 404.
- (141) Truss, R. W.; Han, K. S.; Wallace, J. F.; Geil, P. H. Polym. Eng. Sci. 1980, 20 (11), 747.
- (142) Ramani, K.; Parasnis, N. In *Characterization and Properties of Ultra-High Molecular Weight Polyethylene*; ASTM International: 100 Barr Harbor Drive, PO Box C700, West Conshohocken, PA 19428-2959, 1998; pp 5-5–19.
- (143) Wang, X.-Y.; Li, S.-Y.; Salovey, R. J. Appl. Polym. Sci. 1988, 35 (8), 2165.
- (144) Bellare, A.; Cohen, R. E. Biomaterials 1996, 17 (24), 2325.
- (145) Bastiaansen, C. W. M.; Meyer, H. E. H.; Lemstra, P. J. *Polymer (Guildf)*. **1990**, *31* (8), 1435.
- (146) Zachariades, A. E. Polym. Eng. Sci. 1985, 25 (12), 747.
- (147) Pruitt, L.; Bailey, L. Polymer (Guildf). 1998, 39 (8–9), 1545.
- (148) Changhui, S.; Aibing, H.; Yongqiang, Y.; Di, W.; Jia-kuo, Y. *Int. J. Adv. Manuf. Technol.* **2016**, *85* (5–8), 1217.
- (149) Song, C.; Huang, A.; Yang, Y.; Xiao, Z.; Yu, J. Rapid Prototyp. J. 2017, 23 (6), 1069.
- (150) Khalil, Y.; Kowalski, A.; Hopkinson, N. Manuf. Rev. 2016, 3, 15.
- (151) Khalil, Y.; Kowalski, A.; Hopkinson, N. Addit. Manuf. 2016, 10, 67.
- (152) Goodridge, R. D.; Hague, R. J. M.; Tuck, C. J. *J. Mater. Process. Technol.* **2010**, *210* (1), 72.
- (153) Doi, M.; S.F.Edwards. The theory of polymer dynamics; clarendon Press: Oxford, 1986.
- (154) Talebi, S.; Duchateau, R.; Rastogi, S.; Kaschta, J.; Peters, G. W. M.; Lemstra, P. J. *Macromolecules* **2010**, *4*3 (6), 2780.
- (155) Smith, P.; Chanzy, H.; Rotzinger, B. P. Polym. Commun. 1985, 258.
- (156) Smith, P.; Chanzy, H. D.; Rotzinger, B. P. J. Mater. Sci. 1987, 22 (2), 523.
- (157) Pandey, A.; Champouret, Y.; Rastogi, S. Macromolecules 2011, 44 (12), 4952.
- (158) Rastogi, S.; Lippits, D. R.; Peters, G. W. M.; Graf, R.; Yao, Y.; Spiess, H. W. *Nat. Mater.* **2005**, *4* (8), 635.
- (159) Deplancke, T.; Lame, O.; Rousset, F.; Seguela, R.; Vigier, G. *Macromolecules* **2015**, *48* (15), 5328.
- (160) Deplancke, T.; Lame, O.; Rousset, F.; Aguili, I.; Seguela, R.; Vigier, G. *Macromolecules* **2014**, *47* (1), 197.
- (161) Xue, Y. Q.; Tervoort, T. A.; Lemstra, P. J. Macromolecules 1998, 31 (9), 3075.
- (162) Barham, P. J.; Sadler, D. M. Polymer (Guildf). 1991, 32 (3), 393.

- (163) de Gennes, P. G. C. R. Acad. Sci., Ser. Ilb Mec., Phys., Chim., Astron. **1995**, 321 (9), 363.
- (164) Severn, J. R.; Chadwick, J. C.; Duchateau, R.; Friederichs, N. Chem. Rev. 2005, 105 (11), 4073.
- (165) Hlatky, G. G. Chem. Rev. 2000, 100 (4), 1347.
- (166) Alt, H. G. J. Chem. Soc. Dalt. Trans. 1999, No. 11, 1703.
- (167) Fernandes, J. A.; Girard, A.-L. In *Multimodal Polymers with Supported Catalysts*; 2019; pp 55–80.
- (168) McKenna, T. F.; Soares, J. B. P. Chem. Eng. Sci. 2001, 56 (13), 3931.
- (169) Böhm, L. L. Macromol. Symp. 2001, 173 (1), 53.
- (170) Severn, J. R.; Chadwick, J. C. Dalt. Trans. 2013, 42 (25), 8979.
- (171) Severn, J. R.; Chadwick, J. C. Macromol. Chem. Phys. 2004, 205 (15), 1987.
- (172) Deplancke, T.; Lame, O.; Barrau, S.; Ravi, K.; Dalmas, F. *Polymer (Guildf).* **2017**, *111*, 204.
- (173) Rosehr, A.; Luinstra, G. A. Polym. (United Kingdom) 2017, 120, 164.
- (174) Honda, F.; Honda, H.; Koishi, M. J. Chromatogr. A 1992, 609 (1-2), 49.
- (175) Lecoq, O.; Laurence, G.; Alain, C. Adv. Powder Technol. 2011, 22 (2), 184.
- (176) Otto, C.; Handge, U. A.; Georgopanos, P.; Aschenbrenner, O.; Kerwitz, J.; Abetz, C.; Metze, A. L.; Abetz, V. *Macromol. Mater. Eng.* **2017**, *302* (4), 1.
- (177) Otto, C. Electrically Conductive Composite Materials from Carbon Nanotube Decorated Polymer Powder Particles, University of Hamburg, 2017.
- (178) Forero, S. DE102010013210A1, 2010.
- (179) Murugesan, R.; Orsat, V. Food Bioprocess Technol. 2012, 5 (1), 3.
- (180) Iskandar, F.; Gradon, L.; Okuyama, K. J. Colloid Interface Sci. 2003, 265 (2), 296.
- (181) Wintzheimer, S.; Granath, T.; Oppmann, M.; Kister, T.; Thai, T.; Kraus, T.; Vogel, N.; Mandel, K. ACS Nano **2018**, *12* (6), 5093.
- (182) Bayu, A.; Nandiyanto, D.; Okuyama, K. Adv. Powder Technol. 2011, 22 (1), 1.
- (183) Hopkinson, N.; Hague, R.; Dickens, P. *Rapid Manufacturing: An Industrial Revolution for the Digital Age*; 2005.
- (184) Ngo, T. D.; Kashani, A.; Imbalzano, G.; Nguyen, K. T. Q.; Hui, D. *Compos. Part B Eng.* **2018**, *143* (February), 172.
- (185) Dolenc, A. Software tools for rapid prototyping technologies in manufacturing., Helsinki University of Technology, 1993.
- (186) Hopkinson, N.; Dickens, P. Rapid Prototyp. J. 2001, 7 (4), 197.
- (187) Zhu, X.; Yang, Q. Plast. Rubber Compos. 2020, 49 (3), 116.
- (188) Rimell, J. T.; Marquis, P. M. J. Biomed. Mater. Res. 2000, 53 (4), 414.
- (189) Sigma Aldrich https://www.sigmaaldrich.com/germany.html (accessed Apr 4, 2020).

7. Appendix

7.1 List of hazardous substances according to GHS



Substance	GHS-Pictogram number	H-Statement	P-Statement
Toluene	GHS08, GHS09, GHS02	225, 361d, 304, 373, 315, 336	210, 240, 301+310+330, 302+352, 308+313, 314, 403+233
Ethylene	GHS04, GHS02, GHS07	220, 280, 336	210, 260, 304+340, 315, 377, 371, 405, 403
Pressurized dry air	GHS04	-	-
Triethylaluminum	GHS02, GHS05	250, 260, 314	210, 231+232, 280, 302+334, 303+361+353, 304+340+310, 305+351+338, 370+378, 422
Methylaluminoxane	GHS02, GHS05	250, 260, 314	210, 231+232, 280, 302+334, 303+361+353, 304+340+310, 305+351+338, 370+378, 422
2,6-bis[1-(2,6-diethylphenyl- imino)ethyl]pyridineiron(II)- dichloride	-	-	-
Methanol	GHS06, GHS02, GHS08	225, 331, 311, 301, 370	210, 233, 280, 302+352, 304+340, 308+310, 403+235
Hydrochloric acid	GHS05, GHS07	314, 335, 290	234, 260, 305+351+338, 303+361+353, 304+340, 309+311, 501
2,6-Diacetylpyridine	GHS07	315, 319, 335	261, 305+351+338
2,6-Diethylaniline	GHS07	302	-

Table 2: Hazard statements for the chemicals used in this work¹⁸⁹

Substance	GHS-Pictogram number	H-Statement	P-Statement
Diethyl ether	GHS07, GHS02	224, 302, 336	210, 240, 403+235
Para-Toluene sulfonic acid	GHS07	315, 319, 335	302+352, 304+340, 305+351+338
1-Butanol	GHS05, GHS02, GHS07	226, 302, 318, 315, 35, 336	210, 280, 302+352, 304+340, 305+351+338,
Polyethylene (LLDPE,HDPE)	-	-	-
Allyl bromide	GHS02,GHS05, GHS06, GHS08, GHS09	225, 301, 314, 340, 350, 400	201, 210, 273, 280, 301+310, 305+351+338
Aniline	GHS05, GHS06, GHS08, GHS09	301+311+331, 317, 318, 341, 351, 372, 410	201, 261, 273, 280, 301+310+330
Boron trifluoride diethyl etherate	GHS02, GHS06, GHS08, GHS09	226, 302, 314, 330, 372	260, 280, 284, 305+351+338
Chloroform-d	GHS06, GHS08	302, 315, 319, 351, 373	281, 305+351+338
Ethanol	GHS02	225	210
Iron(II)chloride	GHS05, GHS07	302, 314	280, 305+351+338, 310
Xylene	GHS02, GHS07, GHS08	226, 304, 312+332, 315, 319, 335, 373, 412	210, 261, 273, 301+310, 302+352, 312, 331

Substance	Treatment and quantity	Category
Toluene	~800 L	Toxic for reproduction category 2
Ethylene	~	
Ally bromide	48 mL	Toxic for reproduction category 1B
		Carcinogenic category 1B
Aniline	10 mL	Toxic for reproduction category 2
		Carcinogenic category 2
Chloroform-d	100 mL	Toxic for reproduction category 2
		Carcinogenic category 2

Table 3: CMR substances used in this work.¹⁸⁹

7.2 Supporting Information for: Towards the direct Synthesis of HDPE powders for Powder Bed Fusion based Additive Manufacturing

Supporting Information belonging to the paper entitled:

Towards the direct Synthesis of HDPE powders for Powder Bed Fusion based Additive Manufacturing

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Figure S1. Polymer particles with visible silica cores out of spray dried Ludox-Cl colloidal silica. A: HDPE wax@Silica. B: $10 \mu m$ shell of HDPE. C: Delamination of HDPE from silica core and agglomerations



Figure S2. Yield and silica content in semibatch reactions at various catalyst loadings with **1** heterogenized on 1g of spray dried Perkasil 300 KS (left) and the resulting particle size distributions (right). Reaction conditions: 20° C, 5.4 mmol TEA, 0.72 mmol MAO, 3 bar ethylene, 60 minutes, 200 RPM, 600 mL toluene.



Figure S3. SEM micrographs of polyethylene synthesized with 1 heterogenized on spray dried Perkasil 300 KS with 1.2 μ mol 1. Reaction conditions: 1.2 μ mol 1 with 0.72 mmol MAO on 1 g of support, 20° C, 5.4 mmol of TEA, 3 bar of ethylene, 200 RPM, 600 mL of toluene, 60 min.



Figure S4. Particle size distributions for semibatch reactions at various reaction parameters and work up techniques with 1 heterogenized on 1 g of silica microparticles. Reaction conditions: 4.8 μ mol 1 with 0.72 mmol MAO on 1 g of support, 5.4 mmol TEA, 20 °C, 3 bar ethylene, 60 minutes, 200 RPM, 600 mL toluene/heptane.



Figure S5. Shore hardness D, Young's modulus, ultimate tensile stress and elongation at break plotted against the silica content of HDPE silica composite materials.



Figure S6. SEM micrographs of cryo-break surfaces of a HDPE sample



Figure S7: SEM micrographs of cryo-break surfaces of a with 1.6 wt% silica



Figure S8. SEM micrographs of cryo-broken surfaces of a sample with 11.5 wt% silica



Figure 1. SEM micrographs of commercial HDPE HX11before high energy mixing, *Diamond Plastics*

End of File

7.3 Supporting Information for: Disentangled UHMWPE@silica powders for potential use in Powder Bed Fusion based Additive Manufacturing

Disentangled UHMWPE@silica powders for potential use in Powder Bed Fusion based Additive Manufacturing

Yannick L. Wencke¹, Gerrit A. Luinstra^{1,*}, Rob Duchateau², Friedrich Proes³, Philipp Imgrund³, Jonathan S. Evansen³, Claus Emmelmann³



Figure S1. Samples of disentangled UHMWPE produced with homogenous catalyst action pressed below and over the melting point and subsequently stretched using the "hot shoe technique".



Figure S2. SEM micrographs of cryo-fractured and stretched synthesized UHMWPE samples (from homogeneous catalysis). Left: Disentangled sample pressed below the melting point (125 °C). Right: Entangled sample after pressing at 180 °C (i.e. beyond the melting point)



Figure S3. Preliminary testing in SLS of manually sieved layer of non-templated dUHMWPE. Left: sintering of one layer dUMWPE on black paper; Right: laser sintered part from disentangled UHMWPE



Figure S4. Tensile diagram of UHMWPE and dUHMWPE@silica



Figure S5. SEM micrographs of a cryo-fractured press sintered UHMWPE GUR4150-3 sample

Table S1. Melting temperature and crystallinity values for the synthesized polymer as well as commercial samples.

Sample	1 st melting	2 nd melting	Crystallinity
	temperature	temperature	
	[°C]	[°C]	[%]
dUHMWPE	139.96	137.49	73
GUR 4012	139.63	135.73	59
GUR 4150-3	141.14	130.93	57

Theoretical maximum value of enthalpy for PE used: 293 J/g⁻¹ (B. Wunderlich, Thermal Analysis, Academic Press, New York, 1990)

Table S2. Process	parameters for	preliminar	PBF tests
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Outline	Hatch	Temperatures
Scan speed: 2600 mm.s ⁻¹	Scan speed: 3000 mm.s ⁻¹	Preheating: 120 min
·	·	Processing temperature: 122 °C
Laser power: 36.6 W	Laser power: 36 W	Build chamber temperature: 100 °C

Table S3. Thermal	properties	of dUHMWPE@silica	and GUR 4150-3
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Material	T _{melting} onset [°C]	T _{crystallization} onset [°C]	Sinter window [°C]
GUR4150-3	130.5	115.7	14.8
dUHMWPE	129.8	119.3	10.5
Synthesis of N,N-diallyl aniline



In an inert nitrogen atmosphere, aniline (9.10 mL, 99.7 mmol), allyl bromide (19.9 mL, 230 mmol, 2.3 equiv.) and sodium carbonate (20.5 g, 199,4 mmol, 2 equiv.) were mixed in 320 mL ethanol and 80 mL of deionized water. The mixture was heated under reflux for 16 h. The mixture turned orange. After cooling to room temperature, the mixture was extracted with 4 x 150 mL diethyl ether. The organic phases were united and dried over magnesium sulfate, filtered and the solvent removed *in vacuo*. The residual crude product was purified by vacuum distillation. Boiling point of 77 °C at 2.7 mbar

Yield: 13.9 g, 80.0 mmol, 80%.

¹**H NMR** (400 MHz, CDCl₃): δ [ppm] = 7.23 – 7.18 (m, 2H, H-3), 6.74 – 6.68 (m, 3H, H-2,4), 5.87 (ddt, *J* = 17.1, 10.0, 4.9 Hz, 2H, H-6), 5.22 – 5.14 (m, 4H, H-7), 3.94 – 3.91 (m, 4H, H-5).

¹³**C NMR** (151 MHz, CDCl₃): δ[ppm] = 138.33 (C-1) 130.3 (C-3), 130.3 (C2), 126.5 (C-6), 125.9 (C-4), 122.9 (C-7), 60.0 (C-5).

Synthesis of 2,6-diallyl aniline



N,*N*-diallylamine (1.99 g, 11.5 mmol) were solved in 15 mL xylene and 10 min degassed with nitrogen. Subsequently, BF_3 etherate solution (5.50 mL, 6 M in diethyl ether, 33.0 mmol, 2.9 equiv.) was added with a syringe and the mixture was heated by means of a microwave to 200 °C for 45 min. After cooling to room temperature the brown reaction mixture was added to 150 mL of a saturated sodium bicarbonate solution and mixed for 5 minutes. The reaction mixture was extracted with 3 x 150 mL dichloromethane. The organic fractions were combined, dried over magnesium sulfate, filtered and dried *in vacuo*. The resulting crude product was purified by distillation. Boiling point: 71 °C at 0.95 mbar.

Yield: 1.41 g, 8.14 mmol, 71%.

¹**H NMR** (600 MHz, CDCl₃): δ [ppm] = 7.98 (d, J = 7.5 Hz, 1H, H-3), 6.73 (t, J = 7.5 Hz, 1H, H-4), 5.96 (ddt, J = 16.4, 10.1, 6.2 Hz, 2H, H-6), 5.13 (dq, J = 10.1, 1.6 Hz, 2H, H-7cis), 5.11 (dq, J = 17.1, 1.6 Hz, 2H, H-7trans), 3.35 (m, 4H, H-5).

¹³**C NMR** (151 MHz, CDCl₃): δ [ppm] = 143.4 (C-1), 136.2 (C-6), 128.7 (C-3), 124.17 (C-2), 118.5 (C-4), 116.3 (C-7), 36.5 (C-5).

7.4 Suporting Information for: HDPE@UHMWPE Powders for Power Fusion Based Additive Manufacturing



Supporting Information

for Macromol. Mater. Eng., DOI 10.1002/mame.202100964

HDPE@UHMWPE Powders for Power Bed Fusion Based Additive Manufacturing

Yannick L. Wencke, Friedrich Proes, Phillip Imgrund and Gerrit A. Luinstra*

Supplementary Material belonging to the Paper:

HDPE@UHMWPE powders for Power Bed Fusion based Additive Manufacturing

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Property	Unit	Test method	GHR 8110	GUR 2122	GUR 4012	GUR 4120	GUR 4150-3
Average molecular weight	g/mol	Calculated from VN using Margolies´equation	0.8*10 ⁶	4.2*10 ⁶	1.7*10 ⁶	4.7*10 ⁶	8.1*10 ⁶
Mass melt-flow rate MFR 190/21.6	g/10 min	ISO 1133	1.3	< 0.1	< 0.1	< 0.1	< 0.1
Bulk density	g/cm ³	ISO 60	0.44	0.25	0.45	0.45	0.45
Average particle size (d10)	μm	Laser scattering	70	45	70	65	30
Average particle size (d50)	μm	Laser scattering	120	130	115	120	60
Average particle size (d90)	μm	Laser scattering	220	310	160	210	90

Table S1 Properties of the available UHMWPE powders

Table S2. Particle size distributions for core shell particles with varying amounts of silica on the surface. Reaction conditions see caption of Figure 1

Particles	^x 10,3	^x 16,3	^x 50,3	^x 84,3	^x 90,3	×99,3
	[µm]	[µm]	[µm]	[µm]	[µm]	[µm]
UHMWPE	28.18 ± 0.25	35.33 ± 0.20	59.05 ± 0.35	88.92 ± 0.80	100.41 ± 1.36	156.09 ± 8.32
5 wt% silica	20.48 ± 0.81	28.89 ± 0.73	61.79 ±0.41	94.65 ± 0.78	104.33 ± 0.70	149.87 ±2.65
4 wt% silica	27.87v ± 1.00	37.71 ± 0.96	63.59 ± 0.51	99.24 ± 0.80	109.74 ±1.48	154.85 ±5.35
3 wt% silica	34.59v ± 0.34	43.72 ±0.22	71.91 ± 0.47	105.94 ± 1.34	119.11 ± 1.14	173.83 ±1.99
2 wt% silica	32.25v ± 0.14	41.60 ±0.47	69.39 ± 0.40	102.09 ± 0.68	114.64 ± 1.03	169.47 ± 1.97

Silica content on surface of UHMWPE	Sphericity	
2 wt%	0.89	
3 wt%	0.88	
4 wt%	0.88	
HDPE@silica4@UHMWPE		
Reaction time 15 minutes	0.88	
Reaction time 30 minutes	0.86	
Reaction time 45 minutes	0.86	
Reaction time 60 minutes	0.87	

Table S3. Sphericity	of the synthesized	HDPE@UHMWPE	powders w	ith varying	covering
of silica					

Table S4. Additivation of commercial UHMWPE and HDPE@silica4@UHMWPE composites

Experiment	Polymor motorial	Polymer	Silica nano particles	Carbon black	
Experiment	Polymer material	[g]	[g]	[g]	
Flowability test 0.75% silica	HDPE@silica4@UHMWPE	39.7	0.3	-	
Flowability test 1.25% silica	HDPE@silica4@UHMWPE	39.5	0.5	-	
Flowability test 2.5% silica	HDPE@silica4@UHMWPE	39	1	-	
Flowability test 5% silica	HDPE@silica4@UHMWPE	38	2	-	
PBF test 1% silica	HDPE@silica4@UHMWPE	39.6	0.4	-	
PBF test 1% silica 0.25% carbon black	HDPE@silica4@UHMWPE	39.5	0.4	0.1	
PBF test 1% silica 0.25% carbon black	GUR 4150-3	98.75	1	0.25	



Figure S1. SEM micrographs of silica coated UHMWPE particles. A: 2 wt% silica B: 3 wt% silica C: 4 wt% silica D: 5 wt% silica



Figure S2. SEM micrographs of HDPE@silica5@UHMWPE core shell particles. Reaction conditions of preparation: 8 μ mol/L 1 with 0.84 mL of 1.74 mmol/L MAO on 1 g of silica (5 wt%) coated on UHMWPE, 20° C, 3 bar of ethylene, 200 RPM, 600 mL of toluene containing 9 mmol/L of TEA, 15 min of polymerization time.



Figure S3. SEM micrographs of HDPE@silica5@UHMWPE particles after different attempts of delaminating/ relieving the core shell connection. A: post cryomilling B: post sonification.



Figure S4. Particle size distributions of core shell particles with and without ethylene saturation in 1 L and 10 L reactors.



Figure S5. Tensile diagrams of heat pressed UHMWPE and HDPE@silica5@UHMWPE



Figure S6. Stress-strain curves, Young's modulus, ultimate tensile stress and elongation at break plotted as function of the HDPE content of **injection molded** HDPE@silica4@UHMWPE composite materials.

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Figure S7. SEM micrographs of cryo-fractured, injection molded HDPE@silica 4@UHMWPE tensile bars and HDPE shell of 36 wt%.



Figure S8. Layout of the reduced building chamber filled with nine layers of tensile test specimens each with a different PBF parameter set. Five tensile test specimen of the type 1bb could each be printed in the reduced building chamber filled to maximum capacity with powder. Each set of type 1bb tensile test specimen was connected by thin elements and has a numbered label for easy identification.



Figure S9. A: Smooth powder bed after successful recoating. B: Smeared powder bed after unsuccessful recoating (non-additivated particles).

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Figure S10. Sets of tensile test specimens of the type 1bb built with the best practice parameters. A: HDPE@silica4@UHMWPE with 1 wt% nano silica (top), B: HDPE@silica4@UHMWPE with 1 wt% of nano silica and 0.25 wt% of CB (middle), C: UHMWPE with the addition of 1 wt% of nano silica and 0.25 wt% of CB (bottom)



Figure S11. SEM micrographs of the cryo-fractured, laser sintered tensile test specimens of: HDPE@silica4@UHMWPE (36 wt% HDPE) with 1 wt% of nano silica built by PBF A: of the fracture; B of the top surface.

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Figure S12. SEM micrographs of the cryo-fractured tensile test specimens (side view on top) and its top surface (bottom) of commercial UHMWPE (GUR 4150-3, Celanese) with 1 wt% of nano silica and 0.25 wt% CB built by PBF.

7.5 Declaration of my share in the included publications

Toward the Direct Synthesis of HDPE Powders for Powder Bed Fusion Based Additive Manufacturing

Published in: Macromol. Mater. Eng. 2021, 306 (12), 2100477. Impact factor: 4.367

I declare that I am the first author of this publication. I had the main responsibility for the design and realization of the research project (Conceptualization, Formal analysis, Investigation, Visualization). This included the setting of the objectives, the planning of the experiments, the choice of suitable analytical methods, the evaluation of the analyses, the interpretation of the results and the writing and editing of the manuscript. The publication is a result of a cooperative project with the Fraunhofer Einrichtung für additive Prozesstechnologie (IAPT) as tandem project partner within the framework of the DFG funded SPP2122 Materials for Additive Manufacturing. Friedrich Proes was responsible for the execution of the PBF experiments (Investigation) and supported with writing review and editing as well as visualization. Prof. Dr. Gerrit Luinstra and Dr. Phillip Imgrund were responsible for the setup and availability of the measuring methods, acquiring funding, project supervision/administration and supported the writing and conceptualization of the manuscript

Disentangled UHMWPE@silica powders for potential use in power bed fusion based additive manufacturing

Published in: Eur. Polym. J. 2022, 163 (August 2021), 110936. Impact factor 4.598

I declare that I am the first author of this publication. I had the main responsibility for the design and realization of the research project (Investigation, Formal analysis). This included the setting of the objectives, the planning of the experiments, the choice of suitable analytical methods, the evaluation of the analyses, the interpretation of the results and the writing, reviewing and editing of the manuscript as well as visualization. This publication was again a result of a cooperative project with the Fraunhofer IAPT as tandem project partner within the framework of the DFG funded SPP2122 Materials for Additive Manufacturing. Friedrich Proes and Jonathan S. Evenson were responsible for the execution of the PBF experiments (Investigation) and supported the manuscript with writing review and editing. Prof. Dr. Gerrit Luinstra, Dr. Phillip Imgrund, Prof. Dr. Rob Duchateau and Prof. Dr. Claus Emmelmann were responsible for the setup and availability of the measuring methods, funding acquisition, conceptualization, project administration, supervision and supported the writing and editing of the manuscript

HDPE@UHMWPE Powders for Power Bed Fusion Based Additive Manufacturing

Published in Macromol. Mater. Eng. 2022, 2100964. Impact factor 4.367

This publication is a result of a cooperative project with with the Fraunhofer IAPT as tandem project partner within the framework of the DFG funded SPP2122 Materials for Additive Manufacturing. I declare that I am the first author of this publication. I had the main responsibility for the design and realization of the research project (conceptualization, data curation, investigation, visualization). This included the setting of the objectives, the planning of the experiments, the choice of suitable analytical methods, the evaluation of the analyses, the interpretation of the results and the writing, reviewing and editing of the manuscript. Friedrich Proes was responsible for the execution of the PBF experiments (investigation) and supported the manuscript with writing review and editing as well as data curation and visualization. Prof. Dr. Gerrit Luinstra and Dr. Phillip Imgrund were responsible for the setup and availability of the measuring methods, project administration, funding acquisition, supervision and supported the writing, reviewing and editing of the manuscript.

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9. Declaration on oath

I hereby declare on oath, that I have written the present dissertation by my own and have not used other than the acknowledged resources and aids. The submitted written version corresponds to the version on the electronic storage medium. I hereby declare that I have not previously applied or pursued for a doctorate (Ph.D. studies).

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